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ELECTROCHEMICAL TREATMENT OF MUNICIPAL WASTE WATER

H. C. Miller, et al

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

1 October 1963

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ADVANCED WASTE TREATMENT RESEARCH PROGRAM
U. S. Public Health Service
Contract No. PH 86-62-113

Electrochemical Treatment of Municipal Waste Water

Final Report

H. C. Miller
W. Knipe

Pennsalt Chemicals Corporation
Research and Development Department

October 1, 1963

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FOREWORD

This report was prepared by Pennsalt Chemicals Corporation's Research and Development Department, Wyndmoor, Pennsylvania, under U. S. Public Health Service Contract No. PH 86-62-113. The contract was administered by the Advanced Waste Treatment Research Program, Division of Water Supply and Pollution Control, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio with Mr. Stephen J. Sebesta as Project Officer. Mr. Sebesta was succeeded by Mr. Arthur N. Masse as Project Officer.

The principal scientists working on the project were Mr. H. C. Miller, Group Leader, and Mr. William Knipe, Research Chemist. Analytical services were provided by Pennsalt's Analytical Department under the direction of Dr. Paul A. Munter. The services of a statistician using a Bendix G-15 digital computer, and various engineering services were provided by the Process Development Department under the direction of Dr. Ford Lowdermilk. This report was prepared by Messrs. H. C. Miller and William Knipe and approved by Mr. William M. Lee, Director of the Contract Research Department.

The sewage samples used in this study were furnished through the courtesy of Mr. Robert Bolenius of the Abington Township Sewage Treatment Plant.

ABSTRACT

Although electrolytic methods of treating waste water are reported in the older literature, their effectiveness is in doubt. This study has shown that an electrolytic treatment of secondary effluent from an activated sludge plant using lead dioxide anodes can reduce ABS by 90%, COD by 80%, and chloride by 90%. This treatment has little effect on total solids. The cost of treatment will vary between $.90 and $2.42 per 1000 gallons. The plant costs will vary between 9 and 26 million dollars for a 10 mgd plant. These costs do not include site preparation, roads, landscaping, fences, land area, lighting, laboratories, or other buildings, and the costs depend on the completeness of the treatment and the electrical conductivity of the waste water. The method is not considered economically practical for the Advanced Waste Treatment Research Program, where waters of low conductivity must be processed.

ELECTROCHEMICAL TREATMENT OF MUNICIPAL WASTE WATER

OBJECT: To investigate the possibility of using an electrolytic method for the removal of refractory contaminants from the effluent of municipal sewage treatment plants.

SUMMARY:

1. A literature survey was made on electrolytic methods of treating waste water.

A considerable amount of work was done on electrolytic sewage treatment during the period 1900 to 1930. This work resulted in several electrolytic municipal waste plants but all eventually were abandoned; the reasons given at the time were high cost of operation and questionable efficiency.

Waste water mixed with sea water is now being electrolyzed at two European plants. Good separation of solids at a power cost of about 6 cents per 1000 gallons of waste is claimed at a power cost of 1 cent per KWH.

No work on the electrolytic treatment of municipal waste has been reported in the U. S. in recent years.

2. A procedure was set up to evaluate electrolytic methods of treating samples from the Abington Sewage Plant, Abington, Penna. Standard analytical procedures for COD, ABS, chlorides, and total solids were supplied by the Robert A. Taft Sanitary Engineering Center.

3. The specific conductance was determined for both primary and secondary effluents from the Abington plant.

4. The performance of various electrode materials was evaluated for use in the electrolysis of waste water. Erosion rates and polarization potentials were determined in both secondary effluent and KCl solutions having the same conductance.

5. The standard analytical procedures were modified to work on samples containing hypochlorite. A faster method for the determination of ABS was demonstrated.

6. An apparatus for the pasteurization of secondary effluent by a procedure approved for the Advanced Waste Treatment Research Program was set up.

7. A series of statistically designed experiments was run with selected anode materials to determine optimum conditions of pH, current density, and temperature for the electrolytic treatment of pasteurized secondary effluent.

8. The destruction of bacteria by electrolysis was determined for one electrode system.

9. The effect of sodium hypochlorite and chlorine on the reduction of COD, ABS, and total solids in secondary effluent was determined.

10. Two sizes of cells were run at optimum conditions to yield data on the power requirement and performance of the lead dioxide anode-iron cathode cell.

11. The data were analyzed and estimates made on the cost of the most promising electrolytic process for the treatment of secondary effluent.

CONCLUSIONS:

1. The early electrolytic treatment using iron electrodes in a waste solution treated with lime was probably effective because of the high pH and small amount of hypochlorite formed. There is no evidence that any organic material was decomposed by the electrolytic action.

2. The very low electrical conductivity of the primary and secondary effluent requires very close spacing between the anode and cathode of a cell to electrolyze such solutions, if reasonable power is to be used. This low conductivity eliminates the possible use of a diaphragm-type cell.

3. Electrolytic action may prove a very efficient way to introduce chemicals into waste water. An eroding iron anode can introduce an iron floc uniformly and at a constant rate without the introduction of an anion. A lead dioxide anode can convert chloride ion in a waste solution to hypochlorite ion at a uniform and controlled rate without introducing any new materials into the solution.

4. Iron, lead, magnesium, aluminum, graphite, and copper all erode when made anodic in secondary effluent, and can only be used under special conditions.

5. Lead dioxide, platinum, and platinum-plated titanium do not erode when made anodic in secondary effluent.

6. All electrode materials except lead dioxide worked satisfactorily as cathode in secondary effluent.

7. Graphite, lead dioxide, platinum, and platinum-plated anodes generate significant amounts of hypochlorite when used in secondary effluent.

8. Hypochlorite ion interferes with chloride, ABS and COD determinations. It can be destroyed by H_2O_2 for the ABS determination and by titanous sulfate in the COD analysis.

9. Lead dioxide was shown to be the most effective anode material for the reduction of ABS, COD, and chloride in waste water. It did not lower total solids, suggesting that the treatment did not decompose the dissolved material into volatile material.

10. Electrolysis with a "noble" anode is very effective in the destruction of bacteria.

11. The presence of hypochlorite ion in electrolyzed waste water does not account for the reduction of ABS or COD by the electrolytic treatment.

12. The electrolysis of secondary effluent using lead dioxide anodes and platinum-plated titanium cathodes can reduce the COD by as much as 80%, ABS by as much as 90%, and chloride as much as 90%. Lead dioxide anodes with iron cathodes may be somewhat less efficient in reducing COD. All systems have little effect on total solids.

13. The cost of treating secondary effluent by the electrolytic method will vary between $ .90 and $2.42 per 1000 gallons depending on the completeness of the treatment and the electrical conductivity of the waste water. The plant costs, even with very optimistic assumptions, will vary between $9 and $26 million, for a ten mgd plant.

RECOMMENDATIONS

1. Because of its high cost, the electrochemical treatment of waste water cannot be recommended as a process for the Advanced Waste Treatment Research Program, where waters of low conductivity must be processed.

2. The work by the Lead Industries Association now underway on the use of lead and lead-silver alloys in the treatment of waste waters should be followed. Their results may have application in treating waste waters of high conductivity.

REPORT:

1. Introduction

The purpose of this study was to determine the feasibility of using an electrolytic process to remove, destroy, or render less objectionable the trace dissolved material in sewage effluent, so that this waste water could be re-used.

The effort was not directed toward the development of a system to replace present methods of sewage treatment, but to develop a satisfactory post-treatment process for the removal of the so-called refractory compounds not removed by the conventional sewage treatment. Although many of the refractory compounds found in sewage are known, there are also many which are not known. Therefore, it is not possible to make synthetic waste water samples. In this study, at the suggestion of the Project Officer at the Taft Center, liquid samples were taken from primary and secondary sewage treatment plant streams. The Project Officer also suggested that the effect of the waste water treatment be measured in terms of the standard waste water analytical procedures of chemical oxygen demand (COD), total solids (TS), chloride ion (Cl), and alkylbenzene sulfonate (ABS).

The criterion for satisfactory performance of an electrode system was the degree of lowering of the four quantities, COD, ABS, TS, and chlorides.

Because of the exploratory nature of this project, it was planned that the experimental approach should be to use as much intuition and insight as possible so as to move quickly to those techniques and procedures which give most promising results. Effort was directed toward determining the feasibility of the electrolytic method rather than generating technical or scientific data.

2. Literature Review

During the first quarter of this century electrolytic sewage treatment enjoyed a considerable vogue. The most publicized system was that of C. P. Landreth. Essentially, this method treated raw sewage with lime and electrolyzed it using iron electrodes. The solids were allowed to settle and the effluent discharged. The effluent was described as being clear, odorless and non-putrescent. Several demonstration plants were built and became the center of considerable controversy. Doubt was expressed in the literature about the effectiveness of the method; in fact, some critics questioned whether the system worked at all. It was claimed that the lime treatment and settling produced the same result whether or not the sewage was electrolyzed.

Estimates for large systems indicated that the electrolytic method would cost about double that of systems then in use. This, it is felt, was the real reason the system failed to gain more acceptance. It must be pointed out that the non-electrolytic systems then in use were relatively simple, and when judged against the cost of a modern activated sludge plant this electrolytic system would be competitive costwise. Data on the actual performance of the system does leave some question as to its effectiveness by present standards.

Several electrolytic methods for the treatment of industrial waste have appeared in the patent literature since the twenties but very little has been done on a large scale. Very recently interest has been revived in electrolytic methods. Two groups in Europe, one in Italy and another in Norway, are studying methods using sea water addition to increase the conductivity. The mixed sewage and sea-water is electrolyzed and then discharged into the ocean. The methods show promise, but are not feasible for use where the effluent cannot be discharged directly into the sea.

Appendix II is a discussion of electrolytic systems and Appendix III is a bibliography of the literature on electrolytic sewage treatment.

3. Experimental Work

3.1 Abington Township Sewage Plant

All sewage samples for this study were obtained from the sewage treatment plant of Abington Township, Montgomery County, Pennsylvania. This plant was approved as the source of our waste water by the Project Officer at the Taft Center. The plant serves a population of about 26,000 and receives an average of 2.4 mgd of waste water. This is almost entirely sanitary sewage. A flow diagram is shown in Figure I. The plant uses an activated sludge process.

Raw sewage is passed through a primary settling tank, an aeration tank, and a secondary settling tank. The effluent from the secondary tank is chlorinated and discarded. Waste-activated sludge from the secondary settling tanks is returned to the primary tanks. Sludge from the primaries is taken to two sludge digestion tanks, 75' in diameter and 32' high. They are operated in series, and anaerobic digestion is carried on at temperatures controlled between 95 and 100° F. Sludge is sent to the tanks daily, and the hold-up time for digestion is about 14 days.

Considerable volumes of gas are formed in the digestion tanks. Some of the gas is recirculated to the bottom of the tanks for agitation and the rest is bled off through a water trap and used for heating or is flared.

The supernatant liquid from the sludge digestion tank is returned to the raw sewage inlet. Part of the sludge from the digestion tanks goes to drying beds enclosed in greenhouse-like structures where drying proceeds for about six days. The rest of the sludge goes to a vacuum filter where it is dosed with 5% ferric chloride and 14% lime on the basis of the dry solids. The filtrate is piped back to the raw sewage inlet.

The raw sewage has a BOD of about 260 ppm and suspended solids in the area of 330 ppm. Effluent from the primary tanks has a BOD of about 200 ppm and suspended solids of 250 ppm. Most of the samples for this work were taken from the secondary effluent stream before final chlorination. The BOD at this point is about 40 ppm and suspended solids 30 ppm. A series of 24-hour composites was analyzed and average values obtained were COD, 60 ppm; total solids, 475 ppm; chloride, 50 ppm; and ABS, 8 ppm. All samples regardless of source were filtered through Whatman No. 5 filter paper before use. Specific conductance was in the range 5.5-6.2 x 10^{-4} mho/cm. for primary effluent and 4.75-5.3 x 10^{-4} for secondary effluent. The analyses of several samples of primary and secondary effluent are shown in Table I.

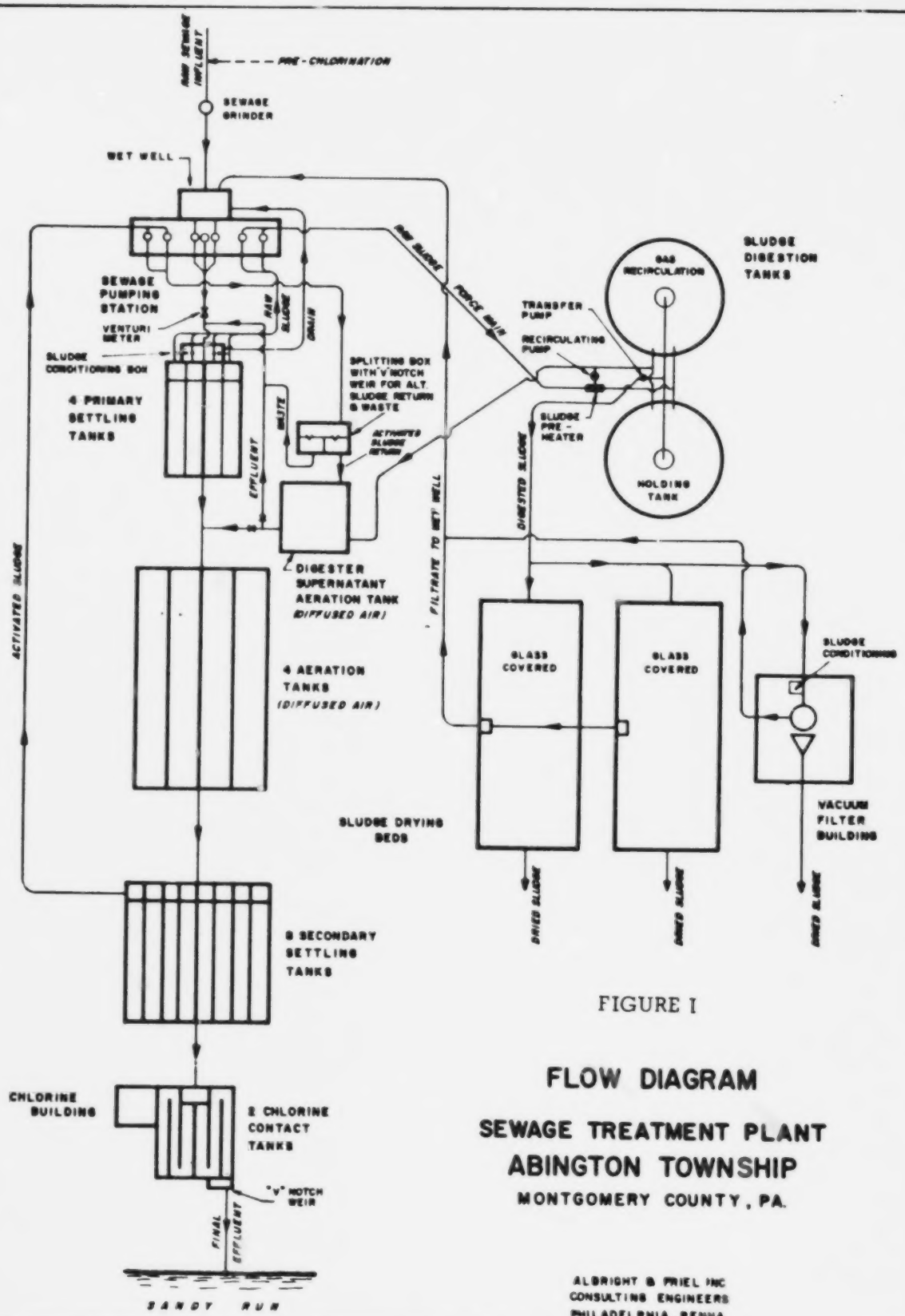

FIGURE I

FLOW DIAGRAM

SEWAGE TREATMENT PLANT
ABINGTON TOWNSHIP
MONTGOMERY COUNTY, PA.

ALBRIGHT & FRIEL INC
CONSULTING ENGINEERS
PHILADELPHIA, PENNA.

TABLE I

Analysis of Abington Township Filtered Sewage Effluent

Date	Type Effluent	Specific Conductance MHOS-CM x 10^4	COD PPM	Total Solids * PPM	Chloride PPM	ABS PPM	pH
5/9/62	Primary	6.09	114	420	46	---	8.1
5/9/62	Secondary	5.19	41	460	48	---	7.5
5/10/62	Primary	5.95	98	450	52	---	8.2
5/10/62	Secondary	5.32	38	490	53	---	7.35
5/11/62	Primary	5.68	82	460	46	---	8.15
5/11/62	Secondary	5.05	47	500	43	---	7.5
5/14/62	Primary	5.82	103	430	42	---	8.1
5/14/62	Secondary	5.05	50	500	48	---	7.45
5/15/62	Primary	6.11	102	450	49	---	8.05
5/15/62	Secondary	5.25	53	540	52	---	7.55
5/16/62	Primary	6.05	101	490	49	---	8.1
5/16/62	Secondary	5.25	64	520	46	---	7.6
5/17/62	Primary	5.75	95	410	50	---	8.15
5/17/62	Secondary	5.19	66	520	52	---	7.7
5/18/62	Primary	5.98	102	440	52	---	8.1
5/18/62	Secondary	5.24	58	470	52	---	7.6
5/21/62	Primary	5.62	103	420	47	---	8.2
5/21/62	Secondary	4.95	62	490	48	---	7.6
5/22/62	Primary	6.30	149	520	55	---	8.1
5/22/62	Secondary	5.28	71	490	50	---	7.9
5/23/62	Secondary	5.56	82	490	52	---	7.8
5/31/62	Secondary	5.4	74	470	51	---	7.5
6/12/62	Secondary	5.05	55	490	50	---	7.2
6/14/62	Secondary	4.51	51	450	42	---	7.3
6/18/62	Secondary	5.07	50	450	46	6.9	7.2
6/19/62	Secondary	5.50	60	460	52	8.7	7.65
6/25/62	Secondary	5.16	45	490	49	6.1	7.4

* These data are for total solids on filtered effluent and represent total dissolved solids. Total solids on unfiltered effluent were not determined in this study, but run about 680 ppm for primary and 520 ppm for secondary effluent for this plant.

3.2 Apparatus and Procedures

All of the electrolyses carried out in this study used direct current which was obtained either from lead storage batteries or from a line-operated power supply which delivered direct current with only a negligible amount of ripple. Voltage and current to the cells were measured with Weston precision meters.

Several types of electrolytic cells were used. In all cases the materials used in their construction were chosen so as not to contribute to the COD of the test solutions. All cells were checked for this possibility by filling them with distilled water and allowing them to stand overnight. In no cases were significant amounts of COD found in the distilled water. Polyethylene, glass, and "Stop-Off"[1], a lacquer material, were used as insulation in the cells.

Figure II shows a typical set-up used in the anode screening tests. The anodes and cathodes alternated in the electrode pack. The active dimension of each electrode was 3" by 3". There were five anodes and six cathodes. Later runs used a system containing only three electrodes, two cathodes, and one anode. These were held about 1/4" apart by polyethylene supports. Systems of more than one-liter volume utilized a circulation system driven by a Gorman-Rupp pump constructed of Buna-N rubber and stainless steel. Electrolyte was withdrawn from the bottom of the cell and returned through a showerhead. This gave an effective distribution over the electrodes and aided in reducing foam levels. Studies using less than a liter of solution were carried out in a beaker stirred with a Teflon-covered stirring bar. Figure III is a typical set-up.

All pH measurements were done with a Leeds and Northrup line-operated laboratory meter. Conductivity measurements were done with a Leeds and Northrup 60 cycle conductivity bridge No. 4688.

All chemicals used were CP grade unless otherwise stated.

The anode screening test used grab samples of raw sewage from the Abington plant. All other tests, unless therein stated, used pasteurized secondary effluent from the Abington plant prepared by the procedure supplied by the Project Officer at Taft and described in Appendix IV of this report. Pasteurized secondary effluent has been observed for over three weeks with little change in its analysis. Analysis for five typical batches is shown in Table II.

---

(1) A product of Michigan Chrome and Chemical Company.

FIGURE II. Grid of Nine Electrodes

FIGURE III. Cell with Magnetic Stirring

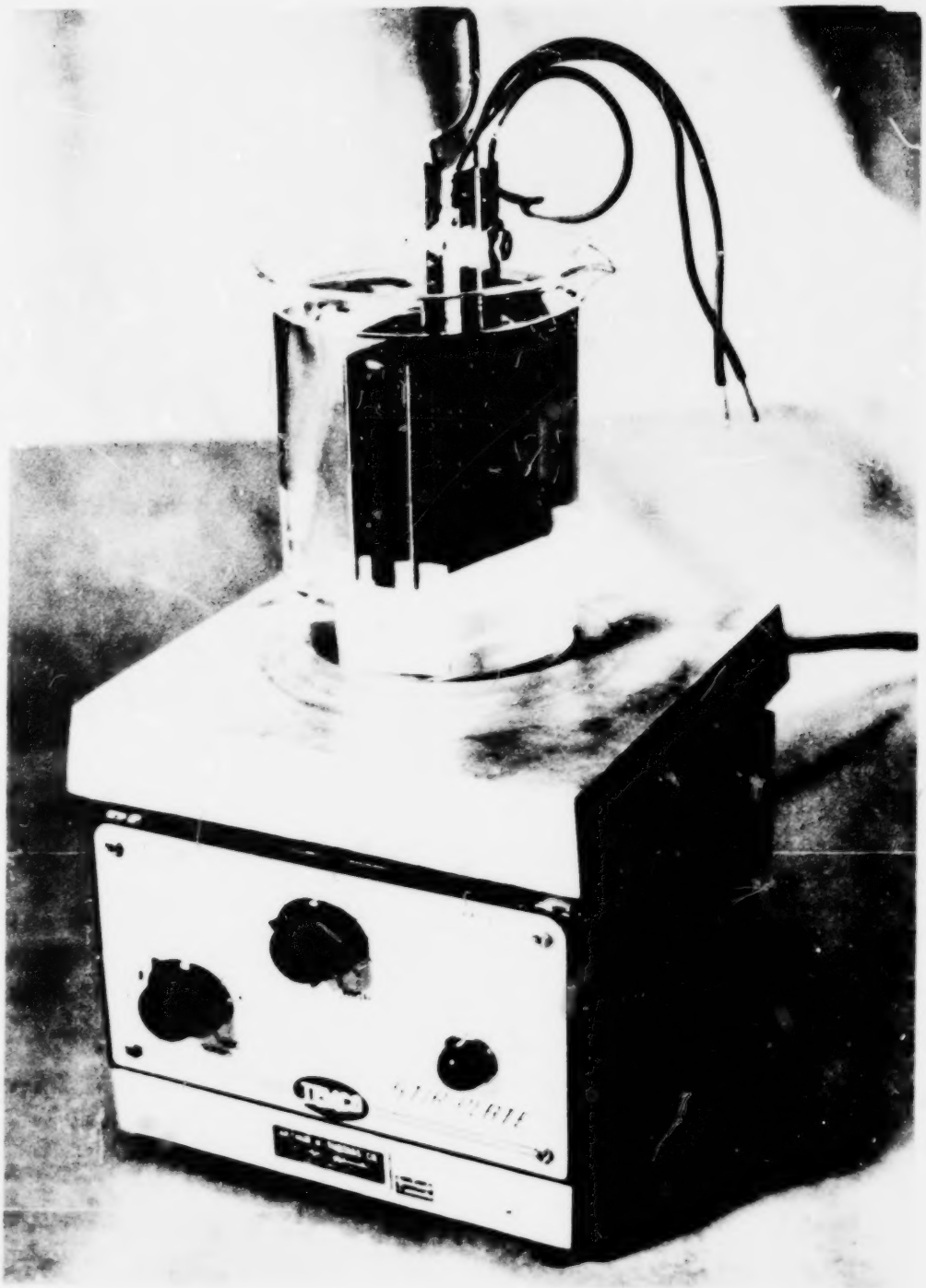

TABLE II

Pasteurized Secondary Effluent
Aging Data

Date of Sample	COD	TS	Cl	ABS	
Batch I	ppm	ppm	ppm	ppm	
12/11/62	48	570	70	7	after pasteurizing
12/18/62	45	560	71	7	" "
12/26/62	50	566	72	7	" "
Batch II					
12/31/62	49	491	75	8	before pasteurizing
1/2/63	57	490	72	9	after pasteurizing
1/7/63	57	491	66	8	" "
1/14/63	67	630	88	8	" "
Batch III					
1/21/63	59	460	58	6	before pasteurizing
1/24/63	59	470	57	7	after pasteurizing
2/4/63	58	460	56	6	" "
Batch IV					
2/13/63	46	420	53	7	before pasteurizing
2/14/63	47	420	55	7	after pasteurizing
2/20/63	49	380	54	6	" "
2/27/63	48	410	49	8	" "
3/7/63	42	400	54	6	" "
3/20/63	39	390	52	7	" "
Batch V					
3/18/63	43	390	49	7	before pasteurizing
3/20/63	50	390	47	8	after pasteurizing
3/27/63	37	390	50	8	" "

Although it has been reported by the Taft Center that this method often precipitates some of the phosphate, we have not had this problem. In fact, no precipitate of any kind has been observed during storage, and only one sample gave an unusual analysis after pasteurizing and storage.

At the start of the project all analytical methods used were standard, either AWWA or Taft methods. The analytical determinations made were the Taft Center's Methylene Blue Method for Determining Alkylbenzene Sulfonate (ABS), and AWWA methods for Chemical Oxygen Demand (COD), Total Dissolved Solids (TS), and Chlorides (Cl). These methods were used exactly as written, with no corrections or changes for any extraneous materials in the samples.

During the fifth month of the project, a Hellige comparator for determing ABS in water was obtained. This instrument was checked against standard samples and against the usual standard method and found to give results within the limits of error of the methods. It was then used in place of the Taft methods, since it was much faster.

During the early screening tests, it became evident that hypochlorite was being formed in the electrolyzed solution. Investigation showed that this hypochlorite (available chlorine) interfered in the total chloride determination, the COD determination, and the ABS determination. Methods overcoming these interferences were worked out and were used from then on. A method for the analysis of available chlorine was also worked out.

Because of the color of the samples treated with graphite anodes, the end point in the Mohr method for the determination of total chloride could not be seen. An amperometric titration apparatus was set up to determine chlorides on these samples.

The presence of chlorate was suspected in some of the electrolyzed material, and a method was developed to determine chlorate content. However, time did not permit a full evaluation of this method.

Three samples were analyzed for: total nitrogen, amino nitrogen, nitrate nitrogen, phosphate, sulfate, calcium, sodium, heavy metals, and loss on heating at 600°C. Methods used were either AWWA or adapted standard methods.

Except for the chlorate method, all new methods were tested fully against standard samples, analyzed unknown samples and prepared synthetic unknown samples. The method was not adopted unless results agreed within the limit of error of the analyses. All of these methods are presented in Appendix I of this report.

3.3 Electrolyte Conductivity and Cell Design.

The measured specific conductance of the secondary effluent from the Abington Township plant was found to range from 4.7×10^{-4} to 5.3×10^{-4} mho/cm. This is about the same conductivity as .003 M KCl solution. This low conductivity places serious restrictions on the electrolytic processes to be used if power comsumption is to be kept within reasonable limits.

Table III lists the voltage of an electrolytic cell using secondary effluent and brackish water as electrolyte at several current densities with electrodes spaced about 0.2" apart. The high voltages at the higher current densities are caused in most part by the voltage drop across the electrolyte. For example, the decomposition voltage of the electrolyte plus normal hydrogen and oxygen overvoltage at 30 ma. per square centimeter is estimated at less than 3.5 volts of the 27.9 volts measured. The remaining 24.4 volts is caused by the resistance drop of the electrolyte. The lower voltage shown in Table III for brackish water electrolyte illustrates the advantage of using highly conductive solution.

It was found that electrode spacing of 1/8" to 1/4" was sufficient to allow good circulation of solution between electrodes, and close enough to keep power requirements within reasonable levels at the lower current densities.

Cells with diaphragms were found to operate at voltage three times higher than those without diaphragms even at very close spacing of the electrodes to the diaphragm. No further work was done with this type cell, because of the excessive power requirements.

Table III

Cell Voltage vs. Current Density for Two Types of Electrolyte

Current Density ma/sq. cm.	Cell Voltage	
	Secondary effluent	Brackish Water[1]
1	3.3	3.2
6	7.8	5.5
30	27.9	14.9

(1) Estimated voltage for a specific conductance of 12×10^{-4} mho/cm. at a salt concentration of 1000 ppm.

3.4 Anode Material Screening

It is well known that the electrode material can influence the course of the electrolytic reaction. Therefore, in this study, electrode materials were chosen that were known to differ in their electrolytic action. Anode materials were considered before cathode materials, because of the greater

probability of decomposing the organic waste by an oxidation reaction, and because of the greater dependence of anodic reaction on the electrode material.

Noble (or inert) anodes, not attacked during electrolysis, are the type of anode of greatest interest to this study. The second type, eroding anodes, have been used in waste treatment and in some cases the eroded metal formed a floc which helped to remove material from solution. However, in most cases an eroding anode would be too expensive for waste treatment. In neutral or acid anolyte platinum, magnetite, graphite, and lead dioxide are likely inert anode materials. In strong alkaline solution, iron and stainless steel should also be inert. Copper, lead, magnesium, and aluminum are of possible interest as eroding electrodes.

In the preliminary tests all of the metals were made up into grids consisting of five anodes and six cathodes as shown in Figure II. The platinum anodes were made by J. Bishop Platinum Works and consisted of 100 microinches of platinum electroplate on a titanium base. This type of electrode is known to have a low chlorine overvoltage and a long life in a salt brine electrolysis. The lead dioxide anodes were prepared in this laboratory and consisted of a thick electroplate of dense lead dioxide on a tantalum screen. Lead dioxide anodes are used to make perchlorates by the electrolysis of a chlorate solution and are known to have a high chlorine overvoltage. In the preliminary tests lead dioxide, carbon and graphite were run in the screening tests in a cell using a single anode with two cathodes as shown in Figure III.

Table IV shows the change in pH, COD, ABS, TS, and chlorides effected by each of the materials as tested. Current densities for all runs were approximately 6 ma/ sq. cm. The steel, copper, lead, magnesium, and aluminum dissolved almost quantitatively with current. The stainless steel was not attacked to as great an extent, but there was some precipitate formed. It is probable that most of the effect shown on COD and ABS for these materials was due to absorption of impurities on the hydrated oxide precipitates. The various types of graphite were all attacked; rather than forming a precipitate, they flaked, leaving fair amounts of particles in suspension. The solutions ranged in color from light brown to black.

By far the most satisfactory materials were lead dioxide and platinum-plated titanium.

On the basis of these results it was decided to limit further investigation to platinum-plated titanium, lead dioxide, and graphite. Graphite was included because it is commonly used in commercial electrolytic processes and it was hoped conditions would be found where it would not be attacked.

The attack on steel, steel alloys, magnesium, aluminum, and graphite was in agreement with published information. The lead-silver alloy is reported to resist attack in sea water at a current density of about 6 ma/ sq. cm. Under these conditions a lead dioxide surface is reported to form which resists further attack. Our preliminary tests did not show this behavior, and since another type of lead dioxide anode was available, no further work was done with the lead silver-alloy.

TABLE IV

Summary of Anode Screening Tests

Anode Material	Time in Hours	pH Before	pH After	% Change COD	% Change Total Solids	% Change Chlorides	% Change ABS	Remarks
430 Stainless Steel	2	7.2	8.3	-29	-22	-8	-40	Seriously
	5	7.6	9.5	-12	-17	-8	-44	Attacked
Copper	2	7.3	9.2	-39	-38	-2	0	Seriously
"	2	7.2	9.5	-32	-33	-9	-29	Attacked
"	5	7.4	10.6	+100	-47	-80	-26	"
Aluminum	2	7.2	9.5	-8	-44	-7	-50	Seriously
"	5	7.3	9.4	+25	-43	0	-63	Attacked
Magnesium	2	7.1	11.1	+13	-51	-7	-63	Seriously
"	5	7.1	11.3	-41	-55	-88	-67	Attacked
Magnesium with foam removal	3-1/4	7.1	11.3	-48	-60	-57	-88	"
Steel	2	7.4	10.7	-30	-57	-7	-72	Seriously
"	5	7.4	10.6	-16	-47	-16	-62	Attacked
Steel with foam removal	2	7.5	10.6	-21	-46	-19	-78	"
Chlorine Cell								
Graphite	2	7.4	7.2	-31	0	-72	-63	Seriously
"	5	7.2	7.0	-31	-20	-78	-56	Attacked
Platinum on Titanium	2	7.2	8.4	-19	+6	-11	-29	No attack
"	5	7.1	5.6	-37	0	-57	-57	"
Platinum with foam removal	2	7.5	8.5	-23	-6	-2	-50	No attack

TABLE IV

Summary of Anode Screening Tests (Cont.)

Anode Material	Time in Hours	pH Before	pH After	% Change COD	% Change Total Solids	% Change Chlorides	ABS	Remarks
Lead Dioxide	2	7.4	7.8	-62	+6	-90	-88	No attack
"	5	7.6	8.4	-26	+8	-97	-85	"
Graphite Type GALX*	2	7.6	6.8	-23	-7	-82	-44	Seriously
	5	7.6	7.0	-31	-23	-86	-56	Attacked
Graphite Type GALX-58 *	2	7.6	6.5	+42	0	-73	-38	Seriously
	5	7.6	7.0	+36	-11	-84	-13	Attacked

* From National Carbon Co.

3.5 Polarization Studies

Polarization measurements were performed on the materials of prime interest to determine any unusual effects they might have as anodes in secondary effluent. This was done with a cell containing a single anode and cathode spaced one inch apart. Polarization measurements were made with a saturated calomel probe and a General Radio electrometer for measuring voltage between the probe and the anode. The probe was located in the center of the anode about 1/32" from its surface. The electrometer was connected to the anode through a separate lead to prevent errors caused by the flow of current. A plot was then made of the anode-to-probe voltage vs. current density. Measurements were first made in 0.003 M KCl solution and then in secondary effluent. Studies were made on platinum-plated titanium, lead dioxide, graphite, steel, aluminum, and type 430 stainless steel anodes, each working with a platinum-plated titanium cathode.

The platinum-plated titanium and the lead dioxide anodes behave as noble electrodes. In the tests using these electrodes very little current was passed until the decomposition potential of the KCl solution was reached. The measured potential was about 1.5 volts, and was the same for all electrodes. At this potential, hydrogen was liberated at the platinum-plated cathode, and a mixture of oxygen and chlorine at the anode. When secondary effluent was substituted for the KCl solution, the same decomposition potential was noted and the slopes of the current density vs. voltage curves were similar, indicating that the dominant reaction taking place in the KCl solution and the effluent was the same. When iron, stainless steel, and aluminum were run, current started to flow at a much lower potential than was noted for the noble anodes, showing that these anodes were being attacked. There were no significant differences in behavior between the KCl solution and the secondary effluent.

The results of the polarization studies are significant in that they show that the decomposition of water and chloride or the solution of metal are the dominant electrode reactions, and that the small amount of organic material present has not had a profound effect on these reactions.

3.6 Statistical Series

Two sets of statistically designed experiments were performed to evaluate the effect of pH, current density, and temperature on several electrode systems. All experiments used a volume of 700 ml. so that results are directly comparable. The electrode systems were all identical, that is, a single anode was placed between two cathodes. Space between the electrodes was .64 cm. The area of the electrode face was 58 sq. cm., so that anode and cathode each had a total area of 116 sq. cm. Figure III shows the graphite anode system, as a typical example of the set-up used.

The pH of the solution was adjusted by the addition of aqueous sodium hydroxide or phosphoric acid. This introduced an error in the total solid determination, but in no case was this over 10%.

The first set of 24 experiments used lead dioxide and National Carbon Company type GALX graphite anodes. Each variable was tested at two levels: pH 6 or 8; temperature, 25-30 or 55-60°C; and current density, 6 or 30 ma/sq. cm. At the 30 ma/ sq. cm. current density, the time of electrolysis was one hour; at the 6 ma /sq. cm. level, the time was five hours. Thus the same quantity of electricity. 12,600 coulombs, was passed through each sample. This ratio of electrical energy to solution volume, 18,000 coulombs per liter, was used in other experiments. A second set of 12 experiments was done using a platinum-plated titanium anode. In this series initial pH was 5 or 8; current densities and temperatures were the same as the first set. Table V shows initial conditions and results for each experiment in both series.

An analysis of the results from the first series shows several significant effects in spite of the scattering of the data. Current density, initial pH and temperature had little effect on the performance of lead dioxide. In some runs chloride was completely removed. COD was often reduced from 60-70 ppm to 5-10 ppm, while ABS was lowered from 8 ppm to as low as 1 ppm. Graphite was attacked under all test conditions, but more severely at elevated temperatures and current densities. The anode flaked off solid particles and colored the solution from brown to black. This color was not removed by filtering with Whatman No. 5 paper. No further work was done with the graphite anodes because of this attack.

Analysis of results from the second series of experiments with platinum-plated titanium anodes showed no significant effect by changes of current density or temperature. The initial pH had a small effect on total dissolved solids. At an initial pH of 8, total solids were decreased by about 20% and final pH was increased. At an initial pH of 5, total solids increased and final pH was lowered. It is possible that acid electrolysis resulted in the oxidation of the organics present to higher molecular weight compounds, such as converting alcohols to the corresponding organic acids. This could account for the increase in total solids. If in alkaline solution, the oxidation proceeds further and partially degrades the compound, the observed decrease in total solids would occur. No precipitates were observed during any of these electrolyses.

TABLE V

Results, First Factorial Series.

Run No.	Anode Mat. *	CD ma/cm^2	T °C	PH Start	PH End	PH Δ	Cl- Start	Cl- End	Cl- Δ
1	Pb	6	25	8	---	----	70	10	-60
2	G	6	55	8	3.3	-4.7	70	44	-26
3	G	6	25	6	3.8	-2.2	70	23	-47
4	Pb	30	25	6	6.2	+0.2	71	23	-48
5	Pb	6	55	6	4.1	-1.9	71	11	-60
6	G	30	55	6	4.2	-1.8	72	41	-31
7	G	30	25	8	6.7	-1.3	72	6	-66
8	Pb	30	55	8	8.2	+0.2	72	12	-60
9	G	30	55	8	6.8	-1.2	72	47	-25
10	Pb	6	25	6	3.6	-2.4	72	15	-57
11	G	30	25	6	6.1	+0.1	72	11	-61
12	Pb	30	25	8	7.6	-0.4	66	9	-58
13	Pb	6	55	8	4.8	-3.2	66	<1	-65+
14	Pb	30	55	6	3.1	-2.9	66	8	-58
15	G	6	25	8	6.0	-2.0	66	32	-34
16	G	6	55	6	2.8	-3.2	57	47	-10
17	Pb	30	55	8	7.1	-0.9	66	9	-57
18	G	30	25	8	7.0	-1.0	66	9	-57
19	G	30	55	6	3.8	-2.2	88	70	-18
20	G	6	25	6	3.2	-2.8	88	47	-41
21	Pb	30	25	6	3.2	-2.8	88	11	-77
22	G	6	55	8	3.0	-5.0	88	47	-41
23	Pb	6	25	8	3.7	-4.3	88	4	-84
24	Pb	6	55	6	3.5	-1.5	88	3	-85

* Pb = PbO_2

G = Graphite

TABLE V (Cont.)

Results, First Factorial Series

Run No.	COD Start	COD End	COD △	TS Start	TS End	TS △	ABS Start	ABS End	ABS △	Color
1	48	12	-36	570	530	-40	7	---	---	H_2O
2	48	163	+115	570	555	-15	7	2	-5	Coffee
3	48	37	-11	570	569	-1	7	2	-5	Yellow
4	45	13	-32	560	541	-19	7	2	-5	H_2O
5	45	11	-34	560	707	+147	7	<1	-6+	H_2O
6	50	126	+76	566	684	+118	7	4	-3	Black
7	50	24	-26	566	571	+5	7	4	-3	Yellow
8	50	0	-50	566	602	+36	7	1	-6	H_2O
9	57	109	+52	490	550	+60	9	5	-4	Tea
10	57	22	-35	490	578	+88	9	1	-8	H_2O
11	57	32	-25	490	582	+92	9	5	-4	Yellow
12	57	9	-48	491	507	+16	8	2	-6	H_2O
13	57	5	-52	491	457	+66	8	<1	-7+	H_2O
14	57	8	-49	491	568	+77	8	<1	-7+	H_2O
15	57	47	-10	491	447	-44	8	3	-5	Yellow
16	59	217	+155	470	73	-397	7	4	-3	Black
17	57	7	-50	491	540	+49	8	1	-7	H_2O
18	57	31	-26	491	500	+9	8	5	-3	H_2O
19	67	74	+7	630	980	+350	8	6	-2	Yellow
20	67	40	-27	630	840	+210	8	4	-4	Yellow
21	67	7	-60	630	480	-150	8	<1	-7+	H_2O
22	67	290	+223	630	660	+30	8	4	-4	Black
23	67	9	-58	630	400	-230	8	<1	-7+	H_2O
24	67	4	-63	630	500	-130	8	<1	-7+	H_2O

Continued next page

TABLE V (Cont.)

Results, Second Factorial Series.

Run No.	Temp °C	C.D. ma/cm^2	pH Start	pH End	pH △	Cl^- Start ppm	Cl^- End ppm	Cl^- △ ppm
1	55	30	5	3.6	-1.4	57	53	-3
2	25	6	8	8.2	+0.2	57	58	+1
3	25	30	8	9.4	+1.4	57	51	-6
4	25	6	5	3.4	-1.6	57	54	-3
5	25	6	8	8.5	+0.5	57	54	-3
6	55	6	5	2.9	-2.1	57	59	+2
7	25	30	5	3.4	-1.6	57	51	-6
8	55	30	8	9.1	+1.1	57	50	-7
9	25	30	8	8.4	+0.4	57	51	-6
10	55	6	8	8.4	+0.4	57	54	-3
11	25	6	5	3.3	-1.7	58	57	-1
12	55	30	5	3.0	-2.0	58	57	-1

TABLE V (Cont.)

Results, Second Factorial Series

Run No.	COD Start ppm	COD End ppm	COD Δ ppm	TS Start ppm	TS End ppm	TS Δ ppm	ABS Start ppm	ABS End ppm	ABS Δ ppm
1	59	24	-35	470	644	+174	7	4	-3
2	59	38	-21	470	348	-122	7	4	-3
3	59	37	-22	470	372	-98	7	4	-3
4	59	41	-18	470	643	+164	7	4	-3
5	59	41	-18	470	360	-110	7	5	-2
6	59	31	-28	470	630	+160	7	2	-5
7	59	37	-22	470	620	+150	7	3	-4
8	59	38	-21	470	410	-60	7	4	-3
9	59	36	-23	470	380	-90	7	3	-4
10	59	28	-31	470	330	-140	7	3	-4
11	56	42	-14	460	630	+170	6	3	-3
12	56	46	-10	460	590	+130	6	4	-2

The data from the statistical studies on lead dioxide and platinum-plated titanium anodes were combined and analyzed. The lead dioxide system gave the best reductions of COD, ABS and chlorides, regardless of initial conditions of pH, current density, and temperature. In no case was it satisfactory for the removal of solids. Platinum-plated titanium was effective in removing solids only in alkaline solution and this averaged around 20%. In general, the independent variables caused, at best, minor effects with the exception of the pH effect on the platinum anode. Appendix V is a complete discussion of the statistical study.

3.7 Systems Using Iron or Iron Alloy Anodes

The early electrolytic systems reported in the literature used iron or plain steel electrodes almost without exception. This was probably due mainly to the economics involved, but in some cases the formation of hydrated iron oxides in the sewage was considered desirable. However, the most widely tested system, that of C.P. Landreth, specifically treated the sewage with lime in order to raise the pH to about 12, where steel will not dissolve during electrolysis. The lime in this system served a two-fold purpose. Not only did it prevent the anodes from dissolving, but it also was quite beneficial in the treatment of the sewage. As stated above, many critics felt that the lime was more effective than the electrolysis. Recent work done by S.G. Grigoropoulos of the Missouri School of Mines demonstrated the removal of ABS from a synthetic waste solution at a pH of about 7 using iron electrodes at a current density of 2 ma / sq. cm.

In order to determine conditions under which iron anodes could be used to treat waste water without being attacked, secondary effluent was electrolyzed using iron electrodes at a pH of 8.4, 11.0, and 12.7. The results of these tests are given in Table VI. At a pH of 11 or under, iron anodes erode with a high current efficiency. The COD, TS, and ABS are lowered. However, at least part of this lowering is caused by material removed by the voluminous precipitate of $Fe(OH)_3$ formed. In a separate test ferric chloride was added to secondary effluent and the pH adjusted so as to precipitate $Fe(OH)_3$. This treatment removed 57% of the ABS with no electrolysis. It was also found that 50% of the ABS could be removed from secondary effluent by adjusting its pH to about 9 and filtering the precipitated calcium phosphate.

At a pH of around 12, iron becomes passive and does not dissolve when made the anode in a waste water solution. Under these conditions the iron anode is effective in lowering COD and ABS. However, it is not as effective as a lead dioxide anode working at a pH of 7.

No further work was done on the iron anode system.

TABLE VI

Iron Anodes in Secondary Effluent.

Run	pH	Percent Change				
		COD	TS	Cl	ABS	
1	8.4	-73	-56	-51	-88	20 hrs. @ 0.1 amp. anode eroded at a C.E. of 91%. Heavy iron floc.
2	11.0	-63	-32	-18	-72	16 hrs. @ 0.1 amp. anode eroded at C.E. of 100%. Iron and phosphate ppt. present.
3	12.7	-53	+370(1)	+5	-72	16 hr. @ 0.1 amp. anode did not erode. Solution saturated with $Ca(OH)_2$. Heavy phosphate ppt.

(1) Increase in TS due to addition of $Ca(OH)_2$.

3.8 Bacteria Kill Studies

The following experiment was performed in order to confirm the reported effectiveness of electrolytic action on killing bacteria.

Raw secondary effluent was electrolyzed using a volume of 1.5 liters in a glass cell with circulation. The electrodes were platinum-plated titanium, 3" x 3". Five cathodes and four anodes were used at a total current of 2 amperes. Samples of electrolyte were taken at 0, 15, 45, and 180 minutes, and all samples were refrigerated until bacterial counts could be made. All counts were started within four hours after the samples were taken.

The results are summarized in Table VII. Electrolysis does substantially reduce the bacteria count. However, even after 14,400 coulombs have passed, some bacteria survive.

3.9 Effect of Cl^- Ion on ABS and COD

Tests indicated that the chloride ion in secondary effluent was being converted to hypochlorite during electrolysis and this was probably having an effect on the ABS present. To verify this a series of experiments was done using synthetic solutions of ABS and KCl whose concentrations were similar to those in secondary effluent. In one series an indifferent salt, K_2SO_4, was used instead of KCl. These solutions were then electrolyzed with a lead dioxide anode. Table VIII is a summary of results. It will be noted that the presence of chloride is not a necessary condition for removal of ABS with the lead dioxide anode.

Samples of secondary effluent were then treated with hypochlorite but not electrolyzed. If the hypochlorite alone is destroying the ABS these samples should show a reduction. Two sets of samples were tested. The first was treated with an excess based on the amount of hypochlorite that would be generated if only hypochlorite were being formed at the anode. This is 3800 ppm of hypochlorite. Two samples were treated: in the first a pH of 8 was maintained and in the second pH 5. Phosphoric acid was used in both to maintain the pH. The ABS was reduced from 8 to 6 ppm; total solids and chloride were greatly increased. COD could not be determined because of the high chloride concentration.

The second set was treated with a more realistic amount of hypochlorite, 100 ppm. The starting pH was 7.5 and after addition of the hypochlorite the pH was 8.2. This had no effect whatever on ABS or COD originally present. Total solids and chloride were somewhat increased. Both sets were stirred for one hour after addition of the hypochlorite and were stored for a minimum of 24 hours before analysis. It is apparent that the hypochlorite alone had little effect on either COD or ABS.

TABLE VII

Bacterial Counts in Electrolytically - Treated Sewage Water

Samples	Coulombs / liter	Standard Plate Count
1. Original	0	1,280,000 per ml.
2. After 15 minutes	1,200	3,600 per ml.
3. After 45 minutes	3,600	1,200 per ml.
4. After 180 minutes	14,400	240 per ml.

Estimation of Coliform Group Density

Samples	Five Fermentation Tubes			MPN per 100 ml.	Limits of MPN	
	10 ml	1ml	0.1 ml		Lower	Upper
Presumptive Test (L. B.)						
1. Original	5/5*	5/5	5/5	Over 1,610		
2. After 15 min.	5/5	5/5	4/5	1,610	390	4,240
3. After 45 min.	5/5	5/5	2/5	542	180	1,405
4. After 180 min.	5/5	5/5	0/5	240	68	754
Confirmed Test (BGLB)						
1. Original	5/5	5/5	5/5	Over 1,610		
2. After 15 min.	4/5	2/5	0/5	22	7	67
3. After 45 min.	1/5	0/5	0/5	2	<0.5	7
4. After 180 min.	0/5	0/5	0/5	0	0	5.9

Legend

* The number in the numerator represents positive tubes, and that in the denominator, the total tubes planted.

MPN - "Most probable number" of coliform group organisms.
L. B. - Lactose Broth
B . G. L. B. - Brilliant Green Lactose Broth

TABLE VIII

Electrolysis of ABS Solutions

Electrolysis of solution containing 55 P. P. M. Cl^- (as KCl) and 10 P. P. M. ABS

Coulombs Passed	Anode Material	Residual, P. P. M. ABS
360	PbO_2	6
1575	PbO_2	5

Electrolysis of solution containing 55 P. P. M. K_2SO_4 and 10 P. P. M. ABS

Coulombs Passed	Anode Material	Residual ABS, P. P. M.
360	PbO_2	9
720	PbO_2	7
1440	PbO_2	6
360	Pt	9
720	Pt	9
1440	Pt	9

A sample of secondary effluent was treated with chlorine. The gas was intermittently bubbled through the solution so as to maintain sufficient free chlorine to give a positive test with starch-potassium iodide paper for one hour. The solution was stored for 24 hours and analyzed. Total solids and chloride were increased. The ABS was reduced 16% and the COD was increased 30%.

Neither a hypochlorite nor a chlorine treatment behaved like the electrolytic treatment of secondary effluent.

3.10 Relation Between ABS and COD

ABS is the only organic constituent of secondary effluent that can easily be quantitatively measured. An attempt was made to determine the relationship between ABS and COD in the course of an electrolysis. A solution containing 20 ppm of ABS only was electrolyzed for a period of 12 hours with a lead dioxide anode at a current of 0.2 amp. Samples were withdrawn periodically and analyzed for ABS and COD. Because of the low current the reaction went very slowly. No correlation between ABS and COD changes was obtained. The measured ABS content decreased only slightly but COD actually increased.

The small decrease in ABS, from 20 to 15 ppm in 12 hours'electrolysis, is worthy of note since the amount and stability of the foam formed by the samples decreases rapidly. For example, after seven hours'electrolysis, analysis still indicated 20 ppm of ABS present but the observed foaming properties of this material were markedly less than the starting solution. Since ABS analysis will include unsubstituted benzene sulfonates or sulfonates with shorter chain substitutents, it appears that the electrolysis is effecting scission of the alkyl chain, leaving residues of lower surface activity.

3.11 Complete Chemical Analysis of Treated and Untreated Secondary Effluent

Total solids, residue at 600°C, available chlorine, chloride, COD, ABS, sulfate, calcium, phosphate, heavy metals, silica, and nitrogen were determined on two five-liter samples of treated unpasteurized secondary effluent and on one sample of untreated material. The electrolysis was carried out in a glass jar using 293 sq. cm. of lead dioxide as anode and an equal area of iron as cathode. (Both electrodes have been used in successive electrolyses with no cleaning or treatment of the electrodes between runs.) The electrolysis was carried out for 205 minutes at a current of 7.3 amperes. The results of this treatment along with those for untreated effluent are shown in Table IX.

TABLE IX

Complete Analysis for Treated and Untreated Secondary Effluent

	Treated		Untreated
	Sample I	Sample II	
Residue at 103°C.(1)	390	450	490
Weight loss in residue at 600°C.	134	140	65
Available Chlorine(2)	<1	<1	<1
Chloride	5	9	66
COD	29	30	60
Sulfate (as SO_4)	63	78	73
Calcium	21	14	35
Phosphate (as P_2O_5)	3	6	28
Heavy metals (as lead)	<1	<1	<1
Silica(3)	3	4	0.6
Ammonia nitrogen (as N)	3	12	16
Total Nitrogen (less NO_3)	6	13	20
Nitrate (as N)	12	11	11
ABS	2	3	10

(1) Residues comprise dissolved non-volatile substances plus suspended solids which pass #5 filter paper. Some insoluble material is undoubtedly lost from the electrolyzed effluent due to (a) slight deposits on electrolysis vessel and (perhaps) on electrodes, and (b) traces retained by filter paper.

(2) Although samples are refrigerated pending analysis, there may be some loss of available chlorine following electrolysis.

(3) The small increase in silica is attributed to conducting the electrolysis in a glass vessel.

The reduction in COD and ABS is typical of these electrolytic treatments. (COD is often reduced further, especially when platinum cathodes are used; however, this varies considerably.)

3.12 Power Requirements

A treatment of 18,000 coulombs per liter was chosen as the constant dose for the statistical study because it was found that the anodes under study all produced substantial effects on most of the variables at this dose. Although there were wide variations in individual runs, the lead dioxide system in some cases produced an 80% lowering of COD, a 90% lowering of Cl, and an 88% lowering of ABS. Since this is a substantial amount of power, and would be a major part of the cost of the treatment, it might be expedient to sacrifice some of the effect by reducing the amount of power used in order to lower cost.

To study this possibility a series of tests was run in which the time of treatment was varied. The standard three-electrode cell with a volume of 700 ml. of secondary effluent, lead dioxide anodes and platinum-plated cathodes was used. A second series was run using the same procedure, but the foam was removed as formed. These results are summarized in Table X, and in Figure IV the results without foam removal are plotted as a function of coulombs passed.

The lower reduction of COD for those runs in the foam skimming series is difficult to explain. When the foam is allowed to remain on the surface, it dries and forms a scum. This scum is then removed in the final filtering before analysis. It may be that some reduction in COD is caused by the material carried out of the solution by this scum. The dried scum was never analyzed. However, analysis of the liquid formed when the skimmed foam from a five-liter electrolysis broke gave a COD of 355 ppm, ABS 60 ppm, TS 330 ppm, and chloride 83 ppm. This was a six-fold concentration of material in the foam, but the amount carried out by the foam was trivial.

Because the effect of foam skimming is not clear from these tests, it was not assumed in the cost estimates. The cost was estimated at two levels of power: 9,000 coulombs per liter where the expected reductions are: COD 65%, ABS 50%, and Cl 65%; and 18,000 coulombs per liter where the expected reductions are: COD 80%, ABS 90%, and Cl 90%.

3.13 Cost of Electrolytic Waste Treatment

Laboratory tests have shown that the best that can be expected from an electrolytic treatment of secondary effluent is a reduction of about 80% in the COD, 90% in chloride, and 90% in ABS. There will be little effect on total solids. This reduction will be achieved by a dose of 68×10^6 coulombs per 1000 gallons. At one-half of this dose, or 34×10^6 coulombs, the COD should be lowered about 65%, ABS 50%, and the chloride 65%.

TABLE X

Time Series

Time in min.	CD ma /cm^2	Coulomb Dose Per liter	% Change				Remarks
			COD	Cl	TS	ABS	
300	6	18,000	-75	-90	-9	-88	Foam not removed
60	30	18,000	-80	-78	-11	-80	"
45	30	13,500	-70	-72	+26	-66	"
30	30	9,000	-68	-65	+21	-50	"
15	30	4,500	-50	-43	+24	-33	"
60	30	18,000	-48	-92	+8	-95	Foam removed
45	30	13,500	-50	-75	+8	-95	"
30	30	9,000	-46	-62	+3	-94	"
15	30	4,500	-40	-45	+3	-84	"
60	6	3,600	-32	-38	+3	-75	"
45	6	2,700	-30	-28	0	-50	"
15	6	900	0	-8	+8	-50	"
16 hours	.86	8,200	-54	-59	-45	-30	Foam not removed

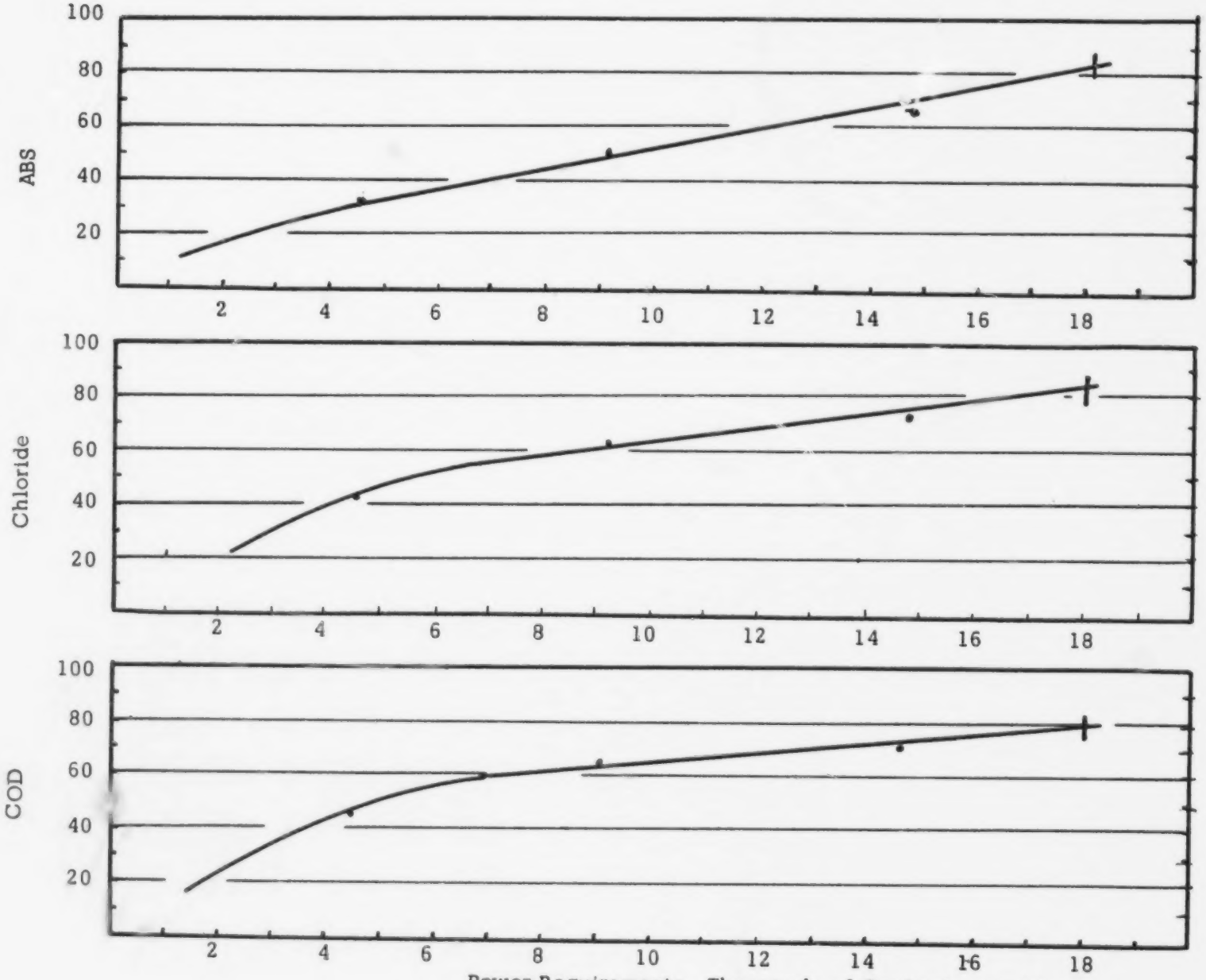

Fig. IV. Effect of Treatment Time on COD, Chlorides, and ABS

The cost of this treatment is largely determined by the amount of electrical power used and the life of the anodes.

An estimate of the cost of treating waste water at two levels of conductivity was made to illustrate the large effect of conductivity on the cost of electrolytic waste treatment. These two levels were 5×10^{-4} and 12×10^{-4} mho/cm. The lower level represents "fresh effluent", and is the typical secondary effluent tested in this study. The higher level, called brackish effluent, would be for a solution with about 1000 ppm of salt.

Both the power consumed and the number of anodes required are dependent on the anode current density. Since the statistical study showed that the performance of the cell was not affected by current density, it is possible to choose an operation point that will minimize the cost without affecting the treatment. This operation point was chosen by plotting estimated power and anode cost versus current density. The following assumptions were used in these estimates:

1. Coulombs/1000 gal. 68×10^6

2. Cell voltage:

Current Density ma/sq. cm.	Volts: Fresh Effluent	Volts: Brackish Effluent*
1	3.3	3.2
6	7.8	5.5
9		6.9
30	27.9	14.9

3. Lead dioxide anode size: 1-1/4" x 6" x 30"

4. Active anode area: 2 sq. ft./anode

5. Anode cost: $20.00 each

6. Anode life: 1000 days

7. Effluent conductivity mho/cm. at 25°C.
   - Fresh effluent: 5×10^{-4}
   - Brackish effluent*: 12×10^{-4}

8. Electrical power: $0.005/KWH

The minimum power and anode cost for the treatment of secondary effluent with a conductivity of 5×10^{-4} mho/cm. and using an anode life of 1000 days is achieved by operating at a current density of about 6 ma/sq. cm. The current density for effluent with a conductivity equal to brackish effluent would be about 9 ma/sq. cm.

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* 1000 ppm NaCl

For the cost estimate a basic unit was taken, consisting of four electrolytic tanks operated in series from a single power supply. For fresh effluent each unit will contain 72,000 1-1/4" x 6" x 30" anodes mounted between steel sheets as cathodes. This unit will be capable of treating 1,000,000 gal per day at the 68×10^6 coulombs per 1000 gal. dose for the maximum effect, or 2,000,000 gal. per day for the somewhat lower treatment. For the brackish effluent, using the same power unit as for the fresh waste, 60,000 1-1/4" x 6" x 30"anodes would be required, and this unit could treat 1,250,000 gal per day at the maximum dose or 2,500,000 gal per day at the lower dose. Plants for 10 and 100 mgd are made by grouping 5 or 50 of these units for the low level or 10 and 100 for the high level fresh effluent treatment. For the brackish effluent where the basic unit is 1.25 mgd the groupings are 4 or 40 for the low level and 8 or 80 for the high level treatment.

Not included in the estimates are a sand filter for the discharge, sites preparation, roads, landscaping, fences, land, area lighting, laboratories or other buildings and the cost of any polishing operations needed to make the product potable. A summary of the cost is given in Table XI. A more detailed breakdown is given in Appendix VI.

TABLE XI
Electrolytic Treatment Cost for Fresh and Brackish Effluent

	Fresh Effluent		Brackish Effluent	
	Low Dose	High Dose	Low Dose	High Dose
Cost per 1000 gal.	$1.21	$2.42	$0.90	$1.80
Plant Costs				
2 mgd	2,700,000	5,260,000	1,906,000*	3,701,000*
2.5 mgd*			2,383,000	4,626,000
10 mgd	12,940,000	25,740,000	9,112,000	18,084,000
100 mgd	128,140,000	256,140,000	89,860,000	179,580,000

* The calculated cost of a 2.5 mgd plant was normalized to 2 mgd by multiplying by 0.8.

3.14 Incomplete Information

During the course of the work the following items were not completely investigated because of lack of time. Information on these subjects would be helpful in the complete evaluation of the electrolytic processes taking place. However, it was felt that in view of the high cost

of the treatment, further work to evaluate these items was not justified:

1. The amount of chloride converted to chlorate. Although some effort was spent in developing a method to determine the chlorate content of the electrolyzed effluent, time did not permit a full evaluation of this procedure.

2. The effect of cathode material in the electrolytic treatment. Only two cathode materials were used in this study, iron and platinum-plated titanium. There may be some evidence that the platinum cathode was a little more effective in reducing the COD than was the iron. Lead is also a possible material.

3. Lead-silver alloys. Lead-silver alloys are reported to form insoluble lead dioxide coats when made anodic in chloride solution. In one trial in this study this behavior was not noted. A more complete investigation might find conditions where these alloys could be used. If so, a considerable saving in anode costs should be possible. The Lead Industries Association study will certainly look into this possibility.

4. Foam removal. It was observed during this study that electrolyte foam is denser than foam formed by mechanical means. This may be caused by rapid diffusion of hydrogen gas through the bubble wall, allowing it to shrink without breaking or by the production of smaller bubbles formed electrolytically rather than by mechanical means. In the laboratory test there appeared to be about a six-fold concentration of impurities in the electrolytic foam. However, the volume of this foam was such that, in the one analysis made, this did not represent a significant removal of impurities from the main body of the liquid. There was considerable scatter of data for foam removal, making its evaluation impossible.

5. Analysis of effluent and foam. Analysis of treated and non-treated secondary effluent are shown in Table IX. The ignition of residue at 600° C shows that treatment diminishes ash, but increases the mass of combustible material. Our only interpretation is that organic materials, for example, polysaccharides, gain weight during electrolysis by addition of oxygen or replacement of hydrogen by oxygen or chlorine. The remarkable reduction in chloride content has been noted in all analyzed runs. A minor amount of chloride may go to chlorate (not included in these values) and some may go to form organic chlorine compounds. We believe most chlorine is lost as such (or as chlorine oxides) in the evolved oxygen and hydrogen. The gases have a strong chlorine odor and react with iodide paper. No quantitative estimate has been made, however.

The large loss in phosphate was unexpected. It may have been removed with the scum formed from the collapsed foam. Foam formed during electrolysis of a separate five-liter run was removed for study. It collapsed to about 100 ml. of liquid, the analysis of which is shown in Table XII.

TABLE XII

Analysis of Electrolytic Foam

	Found in Foam	Change in Treated Effluent if Foam Were Returned
TS	330 ppm	6 ppm
ABS	60 ppm	1 ppm
COD	355 ppm	7 ppm
Chloride	83 ppm	1.5 ppm

APPENDIX I

DISCUSSION OF ANALYTICAL METHODS

APPENDIX I

DISCUSSION OF ANALYTICAL METHODS

When we started doing analytical work for this program, we were given the Taft Center procedure for the determination of ABS and were instructed to use that method solely. At the same time, we were instructed to use the AWWA methods for COD, total dissolved solids and chlorides.

Early in September 1962, after doing development work on a Hellige comparator for the Wissahickon Watershed Assoc., we obtained a Hellige comparator to use for the determination of ABS in sewage. To check this comparator, we ran a series of standards. Results are tabulated below:

ppm ABS taken	ppm ABS found
0.2	0.2
1.0	0.9
2.0	2.0

Many more tests were run with the maximum difference being 0.1 ppm ABS.

At the beginning of October 1962, it was decided to check the original methods to determine if hypochlorite interfered with any of these methods. At this time hypochlorite was shown to be present.

The first investigation was on the determination of available chlorine (hypochlorite). A colorometric method based on o-tolidine was adapted to these samples and standard curves drawn. This method was then used to determine the amount of available chlorine in all subsequent solutions.

Next, the effect of available chlorine on the ABS method was investigated.

ABS present - ppm	$AvCl_2$ present - ppm	ABS found - ppm Taft Procedure
10	10	10
10	50	6
10	100	1

Next, the effect on the Hellige comparator was investigated.

ABS Present - ppm	$AvCl_2$ present - ppm	ABS found - ppm
10	10	9
10	50	No color produced
10	100	" " "

Next, the available chlorine was destroyed by adding caustic soda and peroxide in the cold.

ABS present - ppm	$AvCl_2$ present - ppm	ABS found - ppm Hellige Comparator
2	50	2
10	50	9
10	500	10

Since this seemed to give good results, further tests were run, giving similar checks, that is $\pm$ 0.1 in the 1 to 2 ppm range and $\pm$ 1 in the 10-20 ppm range. The procedure is as follows: Take sample such that there is present less than 50 micrograms ABS, dilute if necessary to 50 ml, add 2 drops of 0.5 N NaOH and 5 drops of 30% H_2O_2. Proceed with Hellige method. If concentration of available chlorine is known to be less than 100 ppm, use only 2 drops of 30% H_2O_2.

The effect of available chlorine on the determination of total chloride was investigated. As a source of available chlorine, a sample of Perchloron was used. This analyzed 70% available chlorine and 48% total chloride. This corresponds to 69% total chloride based on available chlorine. Straight Mohr titrations on dilute solutions gave poor results.

ppm $AvCl_2$ Taken	Equiv. ppm Cl^-	ppm Cl^- found
25	17	6
50	34	9

From previous experience, it was known that the caustic-peroxide treatment worked on macro samples, so the same procedure was tried on dilute samples.

DISCUSSION OF ANALYTICAL METHODS

ppm $AvCl_2$ Taken	Equiv. ppm Cl^-	ppm Cl^- found
0	0	1
25	17	18
50	34	39

Since these results are well within the limits of error of the method, this method was adopted. The procedure is as follows: Add to the sample 2 drops of 0.5 N NaOH and 5 drops of 30% H_2O_2. Heat on the steam bath for 30 minutes. Cool, add 1 gram of $NaHCO_3$ and proceed with the Mohr titration.

The effect of available chlorine on the C.O.D. determination was investigated. Various amounts of available chlorine were added to water and the C. O. D. method run.

$AvCl_2$ added- ppm	Equiv. Cl^- - ppm	$FeSO_4$ Titration
0	0	25.45
100	68	25.50
500	340	25.55

Since the $FeSO_4$ titration should decrease with increase of chloride, it is evident that there is an interference. A method to overcome this interference is given in the following section on COD.

APPENDIX I (Continued)

ANALYSIS FOR COD

The interference of hypochlorite on the determination of COD was investigated. Since it is difficult to decompose hydrogen peroxide completely by heating, and any slight excess would interfere in the determination of COD, the possibility of destroying hypochlorite with hydrogen peroxide was ruled out. (Note that traces of peroxide will not interfere in the Mohr and ABS methods).

It was decided to use titanous sulfate as the reducing agent. The excess of this reagent is very susceptible to air oxidation, even at room temperature. Two drops of the commercial 20% solution furnishes 100% excess for reducing 50 ml of 50 ppm available chlorine.

Results obtained using this method are listed below:

Sample Taken	ppm $AvCl_2$ Added	Drops Ti^{+++} Added	COD Found
50 ml	0	0	65
	0	2	63
	50	2	65
	0	0	63
	0	2	62
	50	2	60

The results are well within the limits of error of the original method. This titanous reduction method will be used on all samples in the future.

In order to check the 0.23 correction factor for chloride in the COD method, several concentrations of chloride were run by this method. The correction factors obtained are listed below:

ppm Cl^- Taken	COD Found	Correction Factor
25	5.2	0.21
50	10.4	0.21
100	22.4	0.22

DETERMINATION OF TOTAL SOLIDS

1. General Discussion

The determination of residue by evaporation may be of limited value for estimating the effect of an effluent on receiving water, but it may be useful as a control in plant operation. A large number of solids crystallize as hydrates, which lose water at various temperatures and form decomposition products before all their water of hydration is given off. This is true also of various colloidal suspensions. In addition, volatile compounds are lost during evaporation and ignition. It is essential for the analyst to understand that the procedure given for residue on evaporation is quite arbitrary and the results generally will not represent the weight of actual dissolved and suspended solids.

2. Procedure for Residue on Evaporation

2.1 Evaporate 100-ml sample in an ignited and tared dish, dry to a constant weight at 103°C, cool in desiccator and weigh. Drying for 1 hr at 103°C is usually sufficient. On samples with a pH below 4.3, NaOH is added and a pH of 4.3 maintained during evaporation. The amount of Na added is subtracted from the weight of residue.

3. Calculation

$$\text{mg/l residue on evaporation} = \frac{\text{mg residue} \times 1{,}000}{\text{ml sample}}$$

DETERMINATION OF DETERGENT CONTENT (ABS)

1. General Discussion

1.1 Principle: This method depends on the formation of a blue colored complex when methylene blue reacts with anionic surfactants in aqueous solutions. This includes not only ABS but other anionic surfactants as well. The complex is extracted with chloroform, and the intensity of color extracted is proportional to the concentration. The intensity of the color is compared to permanent standards in a hand comparator.

1.2 Interferences: Both organic and inorganic compounds can interfere with the determination of ABS. Some of the proved interferences can be predicted on the basis of chemical properties. Organic sulfates, sulfonates, carboxylates, phosphates, and phenols--which complex methylene blue--and inorganic cyanates, chlorides, nitrates, and thiocyanates--which form ion pairs with methylene blue--are among the positive interferences. Organic materials, especially amines, which compete with the methylene blue in the reaction, can cause low results. Positive errors are much more common than negative when determining anionic surfactants in water. It is recognized that interferences can and will exist when using this procedure for determining ABS in sewage effluents. The method is the one of choice for initial screening purposes, because of its relative simplicity and the backlog of experience in its use which has been built up in recent years.

Hypochlorites which may be present interfere by oxidizing the methylene blue. The hypochlorite can be reduced to chloride with hydrogen peroxide in alkaline solution. The slight excess of hydrogen peroxide does not interfere.

2,0 Apparatus

2.1 Pocket comparator. Heilige Pocket Comparator with No. 367-D color disc has been found satisfactory for this purpose.

2.2 Extraction bottle, polyethylene, 4 ounce (Bel-Art #F11637)

2.3 Comparator tubes

3.0 Reagents

3.1 Standard alkylbenzene sulfonate (ABS) stock solution. Weigh an amount of ABS reference material (obtain from The Soap And Detergent Association, New York) equal to 1.000 g ABS on a 100 percent active basis. The ABS content

of the reference material will be specified on each lot. It will generally be in the 55-65 percent ABS range. Transfer quantitatively to a 1,000-ml volumetric flask and add 500 ml of distilled water. Swirl gently until all of the powder is dissolved; let stand for one-half hour or until most of the foam breaks and then dilute to 1,000 ml with distilled water. This solution contains 1.00 mg ABS per ml. To prepare a working standard, dilute 10.00 ml of this stock solution to 1,000 ml with distilled water. The working standard then contains 0.010 mg ABS per ml. The stock solution of ABS is stable for 30 days. The working standard should be made fresh daily.

Methylene blue solution. Dissolve 0.1 g of methylene blue (Eastman Kodak No. P.573 or equivalent) in 100 ml of distilled water. Transfer 30 ml of this solution to a 1000 ml volumetric flask. Add 500 ml of distilled water, 6.8 ml of conc. H_2SO_4 and 50 g of NaH_2PO_4. Shake until solution is complete. Dilute with water to volume.

3.3 Chloroform

3.4 Sodium Hydroxide, approximately 0.5 N

3.5 Hydrogen Peroxide, 30%

4.0 Procedure

4.1 Volume of sample. The volume of sample to be tested is based on the expected ABS concentration. The volume of the sample required can be based on the following:

Expected ABS concentration, PPM	Sample taken, ml
0-2	50
1-10	10
5-20	5
10-50	2
25-100	1

The above concentrations overlap and it is preferred that as small a sample size be taken as is consistent with the above.

DETERMINATION OF DETERGENT CONTENT (ABS)

4.2 Extraction and Color Development

A. Place sample in extraction bottle and dilute to 50 ml with distilled water, if volume is less than 50 ml.

B. Add 0.5 N NaOH dropwise until the solution is alkaline, then add 2 drops in excess. Use pH paper to test for alkalinity. Add 2 drops of 30% H_2O_2 and mix.

C. Add 15 ml of methylene blue solution to the bottle, mix and add 10 ml of chloroform.

D. Squeeze the extraction bottle lightly and, while holding the sides in, replace the cap tightly. Make sure that the small cap on the end of the spout is pressed on firmly before releasing the pressure on the sides of the bottle.

E. Shake vigorously for 30 seconds.

F. Let stand for about 1 minute to permit the chloroform layer to settle out.

4.3 Comparison of Color

A. Wedge a small plug of glass wool in a small funnel and place the funnel in a comparator tube.

B. Remove the small cap from the top of the extraction bottle and transfer the chloroform layer into the comparator tube by filtering through the glass wool in the funnel. This can be accomplished by inverting and squeezing the extraction bottle. Place approximately 5 ml of the chloroform layer in the tube.

C. Place the tube in the right hand opening at the top of the comparator. Fill another tube to the 5 ml mark with distilled water and place in the left-hand opening of the comparator.

D. Make the color comparison immediately while facing directly into north sky daylight or into a diffused fluorescent light. Revolve the color disc so that one standard after another is brought into the observation field.

E. When a color match is obtained with one of the standards, read the results from the color disc. If the color of the unknown is intermediate between 2 glass standards, the true result may be estimated by interpolation.

4.4 Calculation

$$\text{PPM ABS} = \frac{(\text{matched color number})\ (50)}{A}$$

where A is ml of sample taken for comparison.

DETERMINATION OF COD IN PRESENCE OF CHLORIDE

1. General Discussion

The dichromate reflux method has been selected for the oxygen consumed determination because it has been found that this procedure has advantages in reproducibility, applicability to a wide variety of samples, and manipulative advantages over other oxidants.

Hypochlorites interfere and must be converted to chlorides before proceding with the determination. The hypochlorite is reduced to chloride by the addition of titanous sulfate, the excess of which is oxidized by air bubbled through the solution for a very short period of time. The correction factor of 0.23 is then applied to the total chloride content including the original chloride and original available chlorine, but not original chlorate chlorine.

Chlorates interfere but can not be converted to chloride by any simple procedure. Tests have shown that 1 ppm of chlorate shows an apparent COD content of 0.57 ppm. Therefore a correction factor of 0.57 times the chlorate content must be subtracted from the C.O.D., in addition to the chloride correction factor, to give the true C.O.D.

2. Apparatus

2.1 Reflux apparatus: A 300-ml round bottom flask with ground glass neck 24/40 and a Friedrichs condenser.

3. Reagents

3.1 Sulfuric acid, concentrated.

3.2 1:10 Phenanthroline Ferrous Sulfate Solution, 0.025 M. This may be purchased from G. Frederick Smith Co., Columbus, Ohio.

3.3 Standard potassium dichromate solution, 0.05 N; Dissolve 2.4517 g. $K_2Cr_2O_7$, previously dried at 103°C for 2 hr., in distilled water and dilute to 1 liter.

3.4 Standard ferrous ammonium sulfate solution, approximately 0.05N. Dissolve 20 g $FeSO_4(NH_4)_2SO_4.6H_2O$ in approximately 500 ml distilled water. Add 20 ml conc. H_2SO_4 and dilute to 1 liter. This solution must be standardized against the $K_2Cr_2O_7$ daily.

3.5 Standardization procedure: Dilute 25 ml standard dichromate solution to about 250 ml. Add 20 ml conc H_2SO_4 and allow to cool. Titrate against the ferrous ammonium sulfate using 2 or 3 drops of the ferroin indicator.

$$\text{Normality} = \frac{\text{ml } K_2Cr_2O_7 \times 0.25}{\text{ml } FeSO_4(NH_4)_2SO_4}$$

3.6 Titanous sulfate solution, 20%. This may be purchased from LaMotte Chemical Products Co., Baltimore, Maryland.

4. Procedure

4.1 Place 50-ml sample, or an aliquot, diluted to 50 ml with distilled water, in the round-bottomed flask, add 2 drops of the $Ti_2(SO_4)_3$ solution, mix and bubble air through the solution for 15 minutes. If the solution is not purple colored after the addition of the $Ti_2(SO_4)_3$, continue adding the reagent dropwise until the solution is purple, then bubble air through the solution for 15 minutes. Add 25 ml standard dichromate solution. Carefully add 75 ml conc. H_2SO_4, mixing after each addition.

CAUTION: The reflux mixture must be thoroughly mixed before heat is applied. If this is not done, local heating occurs in the bottom of the flask and the mixture may be blown out the side arm of the condenser.

Attach the flask to the Friedrichs condenser and reflux the mixture for 2 hr. Pumice granules or glass beads should be added to the reflux mixture to prevent bumping. Cool and then wash down the condenser with about 25 ml distilled water.

4.2 Transfer the contents to a 500-ml Erlenmeyer flask, washing out the reflux flask 4 to 5 times with distilled water. Dilute the mixture to about 350 ml and titrate the excess dichromate with standard ferrous ammonium sulfate, using 4 drops of phenanthroline indicator. The color change is sharp, changing from a blue-green to a reddish-blue. The end point, however, will not be as sharp as in the standardization of the reagents because of the lower acid concentration. For this reason it is necessary that the sample be diluted to at least 350 ml before the titration is carried out.

4.3 A blank consisting of 50 ml distilled water instead of the sample, togetner with the reagents, is refluxed in the same manner.

5. Calculation

$$\text{mg/l COD} = \frac{(a - b)(N \text{ of } Fe(NH_4)_2(SO_4)_2 \times 8000 - C - D}{\text{ml sample}}$$

Where COD = Chemical oxygen demand

a = ml. of $Fe(NH_4)_2(SO_4)_2$ used for blank

b = ml. of $Fe(NH_4)_2(SO_4)_2$ used for sample

C = Chloride correction = mg/l Cl^- x 0.23

D = Chlorate correction = mg/l ClO_3^- x 0.57

APPENDIX I (Continued)

DETERMINATION OF CHLORIDE (INCLUDING HYPOCHLORITE BUT NOT INCLUDING CHLORATE CHLORINE)

1. General Discussion

1.1 Principle: In this method the chloride, in neutral or weakly alkaline solution containing chromate, is titrated with silver nitrate. Silver chloride precipitates, and at the end point red silver chromate is formed.

1.2 Interference: Iodide and bromide register as equivalent chloride concentration. Phosphate, sulfide, and cyanide interfere. Sulfite interferes but can be removed by treating with hydrogen peroxide.

1.3 If hypochlorite (available chlorine) is present, the amount of chloride equivalent to the hypochlorite is not determined by this method. The hypochlorite must be reduced to chloride by reduction with hydrogen peroxide in an alkaline solution.

2. Reagents

2.1 Standard silver nitrate solution, 0.0141N: Dissolve 2.396 g $AgNO_3$ in 1 liter distilled water. Each ml is equivalent to 0.500 mg Cl. Using the procedure described below, standardize against the standard NaCl solution. The calculation is:

$$\text{Normality of } AgNO_3 = \frac{\text{mg Cl}/35.46}{\text{ml } AgNO_3 - (\text{ml } AgNO_3 \text{ blank})}$$

2.2 Standard sodium chloride solution, 0.0141N: Dissolve 8.243 g NaCl, dried by fusing at 900°C for one-half hour, in water and dilute to 500 ml. Pipet 50 ml into a 1,000 ml volumetric flask and dilute to volume with water. Each ml of this solution contains 0.500 mg Cl.

2.3 Potassium chromate indicator solution: Dissolve 50 g K_2CrO_4 in a little distilled water. Add silver nitrate to produce a slight red precipitate. After it has stood at least overnight, filter and dilute to 1 liter with distilled water.

2.4 Phenolphthalein indicator solution: Dissolve 5 g phenolphthalein in 500 ml ethyl alcohol and add 500 ml distilled water. Then add 0.02N NaOH dropwise until a faint pink color appears.

DETERMINATION OF CHLORIDE (INCLUDING HYPOCHLORITE BUT NOT INCLUDING CHLORATE CHLORINE)

2.5 Sulfuric acid, 1 + 70, approximately 0.5N

2.6 Sodium hydroxide solution, approximately 0.5N: Dissolve 4 g NaOH in 200 distilled water.

2.7 Hydrogen peroxide, 30 per cent.

3. Procedure

3.1 Use 100-ml sample or a suitable aliquot diluted to 100 ml.

3.2 Add approximately 0.5N NaOH dropwise until there are 2 drops in excess. Test with pH paper. Add 2 drops of hydrogen peroxide solution and heat on steam bath for 20 minutes. Cool to room temperature.

3.3 Titration: Either a white porcelain evaporating dish, or an Erlenmeyer flask over white surface should be used. Adjust the sample with either dilute sulfuric acid or sodium hydroxide so that it is just colorless to phenolphthalein. Add 1 ml K_2CrO_4 solution. Titrate with $AgNO_3$ solution until a color change from pure yellow to pinkish-yellow is perceptible. The indicator blank should be determined by titrating distilled water in the same way. This blank, showing the end point color, should be placed near the sample being titrated to aid in the detection of the color change at the chosen end point.

4. Calculation

$$\text{mg/l Cl} = \frac{(\text{ml } AgNO_3 \text{ sample} - \text{ml } AgNO_3 \text{ blank}) \times N \text{ of } AgNO_3 \times 35.46 \times 1{,}000}{\text{ml sample}}$$

APPENDIX I (Continued)

DETERMINATION OF CHLORIDE (INCLUDING HYPOCHLORITE BUT NOT INCLUDING CHLORATE) BY AMPEROMETRIC TITRATION

1. General Discussion

1.1 Principle: In this method the chloride, in a nitric acid solution, is titrated with silver nitrate amperometrically. The electrodes are a saturated calomel electrode (via a potassium nitrate - agar bridge) and a rotating platinum electrode. As the silver nitrate is added, it reacts with any chloride present, forming silver chloride, with very little change in current. Past the end point, the current is proportional to the amount of silver nitrate added. A straight line is found when the current is plotted against the amount of silver nitrate. When this line is extended back, it intersects the line made by the plot of current versus ml before the end point. The intersection of the two lines is at the equivalence point.

1.2 Interference: Iodide and bromide register as equivalent chloride.

1.3 If hypochlorite (available chlorine) is present, the amount of chloride equivalent to the hypochlorite is not determined. The hypochlorite must be reduced to chloride by reduction with hydrogen peroxide in an alkaline solution.

1.4 Colored solutions or insoluble materials do not interfere since the determination is made instrumentally not visually.

2. Apparatus

2.1 Titration apparatus consisting of:

A. Calomel half cell. Prepared by adding a layer of elemental mercury and a layer of solid mercurous chloride to a glass container and then covering with a saturated potassium chloride solution. Contact is made with the mercury through a platinum wire sealed into a glass tube dipping into the mercury. This lead goes to the ammeter.

B. Potassium nitrate - agar bridge. Prepared by adding 3 grams of agar to 100 ml of boiling water, then adding 18 grams of potassium nitrate and boiling for a few minutes. This mixture is added while still hot to a wide U-tube and allowed to cool. This is used as the bridge between the calomel cell and the sample vessel.

C. Rotating platinum electrode. E. H. Sargent S-30421, with lead connected to ammeter.

DETERMINATION OF CHLORIDE (INCLUDING HYPOCHLORITE BUT NOT INCLUDING CHLORATE) BY AMPEROMETRIC TITRATION

D. Microammeter - 0 to 100 μ a -

E. Variable resistor, 2500 ohm, shunted across ammeter.

F. Sample vessel for sample solution and in which is placed the rotating platinum electrode and one end of the U-tube.

3. Reagents

3.1 Standard silver nitrate solution, 0.0141 N. Dissolve 2.396 g. $AgNO_3$ in 1 liter distilled water. Each ml is equivalent to 0.500 mg Cl^-. Using the procedure described below, standardize against the standard NaCl solution. The calculation is:

$$\text{Normality of } AgNO_3 = \frac{\text{mg Cl}/35.46}{\text{ml } AgNO_3 \text{ to end point}}$$

3.2 Standard sodium chloride solution, 0.0141 N. Dissolve 8.243 g. NaCl, dried by fusing at 900°C for one-half hour, in water and dilute to 500 ml. Pipet 50 ml of this solution into a 1000-ml volumetric flask and dilute to volume with water. Each ml of this solution contains 0.500 mg Cl.

3.3 Nitric acid (1:1)

3.4 Methyl orange indicator solution, 0.1%. Dissolve 0.1 gram of methyl orange in 100 ml of water.

3.5 Gelatin solution, 1%. Dissolve 1 gram of gelatin in 100 ml of water; heating, if necessary.

4. Procedure

4.1 Transfer 100 ml of sample (or a suitable aliquot) to titration vessel. Add 2 drops of methyl orange indicator and then add HNO_3 dropwise until solution is just acid. Add 2 drops of HNO_3 in excess. Dilute to approximately 200 ml with water and add 10 ml of gelatin solution.

DETERMINATION OF CHLORIDE (INCLUDING HYPOCHLORITE BUT NOT INCLUDING CHLORATE) BY AMPEROMETRIC TITRATION

4.2 Start the stirring motor, adjust the ammeter to read approximately 20 microamps, and add approximately 2 ml of standard 0.1 N $AgNO_3$. Record volume of $AgNO_3$ added and meter reading obtained. Keep adding $AgNO_3$ in approximately 2-ml portions, recording volume of $AgNO_3$ and meter reading after each addition.

4.3 As the $AgNO_3$ is first added, the meter reading will change only slightly, but after the equivalence point it will increase substantially after each addition of $AgNO_3$. Obtain at least 5 readings after this point has been passed, but do not allow meter reading to go over 90.

If reading on meter approaches 80 before the equivalence point, reduce the noted value to exactly one-half by means of the variable shunt, and then continue the titration.

4.4 Plot the ml of $AgNO_3$ versus the meter readings. Draw 2 straight lines, one through the points before the equivalence point, and one through the points after the equivalence point. Neglect those points near the equivalence point. The equivalence point is taken as the intersection of the 2 lines.

5. Calculation

$$\text{mg per liter } Cl^- = \frac{(\text{ml of } AgNO_3 \text{ at equiv. pt.}) \times N \text{ of } AgNO_3 \times 35.46 \times 1000}{\text{ml of sample}}$$

APPENDIX I (Continued)

DETERMINATION OF AVAILABLE CHLORINE (RESIDUAL CHLORINE)

1. General Discussion

1.1 The orthotolidine method measures both the free and combined available chlorine. If it is desired to determine whether the chlorine is present in free or combined form the flash test or the OTA test may be used.

1.2 To obtain the correct color development with chlorine and orthotolidine (a) the solution must be at pH 1.3 or lower during the contact period; (b) the ratio of orthotolidine to chlorine (both by weight) must be at least 3:1; and (c) the chlorine concentration must not exceed 10 mg per liter.

Commercially available orthotolidine dihydrochloride is considerably purer than the free orthotolidine base. Moreover, the dihydrochloride readily dissolves in water, which makes it easier to prepare the test reagent.

The concentration of the acid in the orthotolidine reagent must be such that it will produce a suitable pH even if the sample has up to 1,000 mg per liter of alkalinity.

To insure a pH of 1.3 or lower and a ratio of orthotolidine to chlorine of at least 3:1, the reagent must be placed in the cell first, and the sample is added to it.

A 6-month stability limit is specified for the orthotolidine reagent as an arbitrary precaution against any discoloration or precipitation due to occasional exposure to high temperatures or direct sunlight. A caution against permitting the reagent to come in contact with rubber is based on observations that significant amounts of reducing substances are extracted from some types of rubber closures by orthotolidine reagent.

1.3 The reaction time and the temperature specified were selected to permit measurement of a maximum proportion of the combined available chlorine present while minimizing loss of color by fading or increase of color due to interfering oxidizing agents which react slowly with orthotolidine, such as nitrites, ferric iron, and certain compounds formed by chlorine with organic matter.

DETERMINATION OF AVAILABLE CHLORINE (RESIDUAL CHLORINE)

1.4 The method given for preparation of zero-chlorine-demand water was selected for convenience; although ammonia-free water is not required, the preference expressed for it is based on difficulties encountered in removing large amounts of ammonia with chlorine alone. Due to the rapidity with which this water may absorb some laboratory fumes, it should be examined for nitrite, chlorine, and reducing agents immediately before use when determining very low concentrations of chlorine.

Excellent accuracy in determination of residual chlorine withorthotolidine may be obtained by photometric methods.

1.6 Interference: When orthotolidine is used to measure residual chlorine, the analyst must satisfy himself as to the presence and the amount of interfering substances in the sample to be tested. Such interferences include nitrite, ferric compounds, manganic compounds, and possibly, organic iron compounds, lignocellulose and algae. The effect of these substances is to increase the apparent residual chlorine content of the sample under examination.

Suspended matter interferes and should be removed by centrifuging prior to test.

2. Apparatus

2.1 Photometer, Leitz, 1 cm light path, 415 mμ filter .

3. Reagents

3.1 Orthotolidine reagent: Dissolve 1.35 g orthotolidine dihydrochloride in 500 ml distilled water. Add this solution, with constant stirring, to 500 ml dilute HCl made by mixing 350 ml distilled water and 150 ml conc. HCl.

Storage: The orthotolidine reagent should be: (a) stored in amber bottles or in the dark, (b) protected at all times from direct sunlight, (c) used no longer than 6 months, (d) kept from contact with rubber, and (e) maintained at normal temperatures. At temperatures below 0 °C, the orthotolidine will precipitate from solution and cannot be redissolved easily. The use of a reagent from which part of the orthotolidine has precipitated may lead to errors due to a deficiency of orthotolidine.

3.2 Pennsalt Perchloron

4. Preparation of Calibration Curve

4.1 Preparation of standard chlorine solution.

A. Determine the available chlorine content of the Pennsalt Perchloron using Pennsalt Standard Method S-47.

B. Transfer to a large glass mortar and pestle an accurately weighed amount of this material such that there is present exactly 5.000 g of available chlorine.

C. Add 50 ml of water to the mortar and triturate the material until a smooth paste is obtained. Let settle for a short time and decant the supernatant material into a 500-ml volumetric flask. Add another 50 ml of water to the mortar and repeat. Keep repeating this procedure until all solids are transfered to the flask. Dilute to volume with water and mix well. (1 ml $\Leftrightarrow$ 10 mg Av.Cl_2).

D. Immediately pipet 10 ml of well mixed solution into a 1000-ml volumetric flask. Dilute to volume with water and mix well. (1 ml $\Leftrightarrow$ 100 γ Av.Cl_2).

E. Immediately pipet 10 ml of well mixed solution (from D) into a 1000-ml volumetric flask. Dilute to volume with water and mix well. (1 ml $\Leftrightarrow$ 1 γ Av.Cl_2).

4.2 Preparation of Curve

A. Pipet 5 ml of orthotolidine solution into a 100-ml volumetric flask.

B. Pipet 50 ml (50 γ Av. Cl_2) of standard chlorine solution (4.1 E) into the flask. Dilute to volume with water and mix well.

C. Within 5 minutes determine transmittance of solution on Leitz Photometer, using 415 mμ filter and 1 cm cell.

D. Repeat 4.2 B with 40, 20, 10 and 0 ml of the standard chlorine solution (4.1 E).

E. Plot the transmittance of each solution versus the number of micrograms of available chlorine present per 100 ml volume.

5. Procedure

5.1 Pipet 5 ml of orthotolidine solution into a 100-ml volumetric flask.

5.2 Pipet 50 ml of the sample into the flask. Dilute to volume with water and mix well.

5.3 Within 5 minutes determine transmittance of solution on Leitz Photrometer, using 415 mμ filter and 1-cm cell. If transmittance value is too low to be found on curve, repeat 5.2 with smaller sample.

5.4 From calibration curve, determine number of micrograms of available chlorine present.

6. Calculations

$$\text{PPM.Av.Cl}_2 = \frac{\text{micrograms AvCl}_2 \text{ present}}{\text{ml. sample}}$$

APPENDIX I (Continued)

DETERMINATION OF CHLORATE CONTENT

1. General Discussion

During the electrolysis of sewage effluents, some chlorate may form from the chloride present in the solution. Since this interferes in the COD determination, it must be determined and corrected for.

1.1 Interferences

Hypochlorites interfere and must be determined and corrected for.

2. Reagents

2.1 Sodium bromide.

2.2 Hydrochloric acid, concentrated.

2.3 Potassium iodide solution, 10%. Dissolve 10 g of KI in water and dilute to 100 ml.

2.4 Starch solution. Triturate 1 g of soluble starch in a small amount of distilled water. Pour this emulsion into 100 ml of boiling distilled water, stir and cool. Starch should be made fresh daily.

2.5 Standard sodium thiosulfate solution, approximately 0.1N. Dissolve 24.82 g of $Na_2S_2O_3 \cdot 5H_2O$ in boiled and cooled distilled water and dilute to 1 liter with the same water.

Standardization: Weigh accurately about 0.21 g of primary standard $K_2Cr_2O_7$ and dissolve in 100 ml of water in a 500-ml iodine flask. Add 3 g of KI, 2 g $NaHCO_3$ and 5 ml HCl. Stopper the flask, mix well and let stand in the dark for 10 minutes. Titrate with the $Na_2S_2O_3$ until there is only a faint yellow color in the solution, add 2 ml of starch solution and continue titration to the disappearance of the blue color. Restandardize weekly. Calculation:

$$N \text{ of } Na_2S_2O_3 = \frac{g \text{ of } K_2Cr_2O_7}{ml \text{ of } Na_2S_2O_3 \times 0.04904}$$

2.6 Standard sodium thiosulfate solution, approximately 0.01N. Pipet 10 ml of the 0.1 N solution into a 100-ml volumetric flask and dilute to volume with boiled, cooled distilled water. The normality of this solution is exactly 0.1 times the normality of the standardized 0.1 N $Na_2S_2O_3$.

DETERMINATION OF CHLORATE CONTENT

3. Procedure

3.1 Pipet 25 ml of the sample into a 250-ml iodine flask.

3.2 Add approximately 1 g. of solid NaBr to the flask.

3.3 Rapidly add 25 ml of HCl and stopper the flask immediately.

3.4 Let stand in the dark for 15 minutes, shaking occasionally.

3.5 Add 2 ml of KI solution around stopper and allow the KI to run into the flask without allowing any vapors to escape.

3.6 Add 2 ml of starch solution and titrate with 0.01 N $Na_2S_2O_3$ to the disappearance of the blue color.

4. Calculation

$$\text{PPM } ClO_3^- = \frac{(\text{ml of } Na_2S_2O_3)\ (\text{N of } Na_2S_2O_3)\ (13900) - C}{25}$$

where C = correction for available chlorine content = $(0.392)(\text{ppmAv}Cl_2)$

APPENDIX II

LITERATURE REVIEW

APPENDIX II
A Survey of the Published Work on Electrolytic Treatment of Sewage and Waste Water

This survey covers both patent and technical literature in the field of electrolytic sewage and industrial waste treatment. Sewage will be defined as that material originating in homes and the like consisting primarily of human excretions. Waste is material arising from industrial processes. It is recognized that industrial wastes are often dumped into the sanitary sewage system and the resultant mixture processed in the local sewage treatment plant. The survey was made by searching Chemical Abstracts, Industrial Arts Index, and the patent art. The original article was read for all pertinent references unless otherwise noted. All references found are tabulated in an annotated bibliography attached to this report. All methods reported are described in detail below.

The earliest record found of electrolytic sewage treatment is a patent[1] issued to William Webster in 1889. The sewage was electrolyzed with iron electrodes at a potential of about 10 volts. If insufficient chlorides were present to generate chlorine, sea water or salt was added. Iron electrodes were specified to take advantage of the formation of hydrated iron oxides which aided in sludge flocculation. A plant was built at Crossness, a suburb of London, England, but apparently nothing further was done.

In 1909, J. T. Harris received a patent[2] on a method for the purification of waste water by electrolysis. This system is unique in that both iron and aluminum are used together as anodes and are allowed to corrode during electrolysis. It was claimed that if either metal is used alone it can not be completely precipitated; however, almost complete removal of metal ions can be achieved with the combination, and better clarification of the solution was obtained. Copper is employed to aid in sterilization. A small electrode, either anode or cathode, is claimed to be sufficient and doesn't add harmful amounts of copper to the solution. This multiple metal system is of interest as a means of introducing metal hydroxides to aid in sludge flocculation.

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1) U. S. 398,101
2) U. S. 937,210

In 1913, G. W. Swinburne received a patent[3] for a method of purifying sewage by electrolysis. The patent did not specify a particular type of apparatus, but required that a chloride be added and the solution be electrolyzed. No fixed amount of chloride was called for, only that sufficient amount be added to give the "degree of purification desired." Apparently a system was never set up, since no further mention is made in the literature.

Although electrolytic sewage treatment plants were in operation as early as 1911 in Santa Monica, Calif. and Oklahoma City, Okla., much of the technical literature and about half of the patents concerning electrolytic sewage treatment in the U. S. are related to the system patented[4] and promoted by C. P. Landreth. The apparatus consisted of a rectangular wooden box containing many vertical steel plates about 1/2 -inch apart and so arranged that the sewage flowed in thin sheets between them. The plates were alternately connected to the positive and negative terminals of a D. C. power supply. The exact number of electrodes varied but one demonstration unit built at Elmhurst, New York City, contained 1100 electrodes 10 by 16 by 3/16 inches. The space between the plates contained paddles mounted on shafts passing through and insulated from the electrodes. The paddles were rotated to assure thorough mixing of the solutions, to prevent polarization of the electrodes, and to remove any scum formed on the electrodes. Electrodes were made of steel but other metals could be used. The power required was determined by the conductivity of the sewage and the condition of the electrodes, since with use the required power increased. The sewage was dosed with lime just prior to entering the electrolyzer. This served to increase the conductivity of the sewage and raise the pH, which passivated the steel, making it erode more slowly, and also aided in settling of solids after electrolysis. Residence time was about one minute but varied from unit to unit depending on size. The effluent from the electrolyzer was run into settling tanks and then discharged. It has been described as being clear, odorless and non-putrescent. (Present laboratory work has shown electrolyzed secondary effluent from an activated sludge plant to be odorless, and often perfectly clear. It is well known that very good bacteria kills can be obtained by electrolysis. See page 23 of this report, for a bacteriological study carried out in this laboratory.)

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3) U. S. 1.079,377
4) U. S. 1,090,893
U. S. 1,131,067
U. S. 1,139,778
U. S. 1,146,942
U. S. 1,222,637
U. S. 1,378,120

The active promotion of electrolytic sewage treatment by Landreth aroused considerable controversy. As stated above, electrolytic plants had been in operation as early as 1911 and good results were reported. The system was claimed to be ideally suited for built-up areas because of the small land requirements and the absence of odor compared to conventional plants. Demonstration plants were built in the Elmhurst section of New York City, Allentown and Easton, Penna., among others[5].

All of these plants were praised at first for their supposedly high quality effluent and lack of odor. Some reservations were made on operating cost since sludge from the settling tanks had to be hauled away and this increased the overall cost. Compared to present day activated sludge plants, this might not be an objection. In time, however, all of the plants were abandoned. It was claimed that the electrolysis did nothing that could not be achieved by dosing with lime at the rate prescribed for electrolysis. The data given in reports on the several plants are not in agreement on the efficiency of this method. The oxygen demand and total solids vary, as would be expected, from plant to plant. In most cases the total solids increase probably from the addition of large amounts of lime. The result of the controversy was that all electrolytic treatment plants had been abandoned by about 1930. No doubt the single biggest factor was the cost of operation, which was estimated to be as much as double that of more conventional methods[6].

In 1930 an electrolytic method of removing grease from sewage was patented[7]. It consisted of a concrete conduit 6 feet deep by 9 feet wide and 150 feet long. There were two sets of electrodes, spaced about 100 feet apart. The anodes comprised closely spaced graphite rods and the cathodes were steel plates. The anode and cathode were two inches apart and the steel plate cathodes abutted alternate walls. The through-put of the system was 7 mgd since the electrodes were so closely spaced the velocity was very high in the electrode area. It is stated that the grease in the sewage coalesced into a hard odorless layer in the areas between electrodes. Despite this apparently successful operation, no further report of this process can be found.

A report[8] was made on preliminary studies carried out in the Soviet Union on an electrolytic method of treating sewage. Experiments were carried out on a laboratory scale using iron and graphite electrodes. Various combinations of single and multiple electrode systems with and without diaphragms were tested. The main work was carried out on stationary systems.

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5) Eng. News-Record, 83, 569-73 (1919); 97, 522-4 (1926). Municipal Journal, 39 551-4(1915).
6) Eng. News-Record, 89, 658-9 (1922).
7) U. S. 1,746,964
8) Dolivo-Dolrovol'skii, L. B., Microbiologiya 6(4) 298 (1937).

Since this study was done primarily to explore the possibility of substituting electrolysis for chlorination in sewage treatment, the main effort was directed towards bacteria kill. Satisfactory results were obtained in a diaphragm cell with sewage in the anode compartment and water in the cathode compartment. It is stated that the method was to be scaled up, but no further report could be found in the literature.

Some work has been done on industrial waste treatment. C. J. Brockman has received two patents[9] for the electrolytic treatment of "whole slop" from alcohol fermentation. These patents are primarily concerned with the coagulation and recovery of solids in the slop. An electrolytic process for the removal of phenolic material, thiosulfates, thiocyanates and chlorides has been described.[10] No specification of the cell is made other than electrode material. Platinum mesh anode and iron mesh cathode are preferred.

Two methods for the removal of cyanides from plating wastes have been patented. The first[11] involves D. C. electrolysis at 93° C and fairly high current densities. It is claimed that concentrated solutions of cyanides can be reduced to several parts per million in a period varying from several hours to several days depending on concentration and composition of the solution. Electrode material is not specified. The second method[12] varies somewhat from the above in that the electrolysis is carried out at ambient temperature. Also, the anode is constructed of porous carbon, and air or oxygen diffusing through the carbon assists in oxidation of the cyanide. It is possible that a system such as this could be of use in the electrolytic treatment of sewage.

Recently, work has begun in Europe on the electrolysis of sewage mixed with sea-water. The object is to utilize compounds present in the sea water; hypochlorite is generated and magnesium salts present form precipitates which aid in sludge flocculation. Not much detail is given[13] on the system currently in use in Norway but a cost of 6 cents per 1000 gallons of sewage treated is claimed with a residence time of less than one hour and using power at one cent per KWH. In a pilot unit at the University of Naples,[14] horizontal electrodes without diaphragms are used. The Naples unit used about one-third sea water and, with a residence time of 10 seconds or less, lowers the BOD to about two-thirds of its initial value. Work is apparently still under way on the Italian system, and a patent[15] has just been issued for the Norwegian method.

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9) U. S. Patents 2,275,217 and 2,334,063
10) Brit. Patent 888,654
11) U. S. Paten 2,520,703
12) U. S. Paten 2,773,025
13) British Chem. Eng. Nov. 1961 Vol 6, No. 111, p. 754
14) C. A. 57, 10950 (1962)
15) U. S. Paten 3,035,992

APPENDIX III

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APPENDIX III

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4- Municipal Engineering, 41, 461 (1911). Description of plant at Oklahoma City, Okla. (1)

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6- Collier, W. R., Engineering Record, 66, 55 (1912) Description of plants at Oklahoma City, Okla. and Santa Monica, Calif. (1)

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1) Reviewed for survey
2) Not available or not reviewed
3) Copy in project files and reviewed

Part II Patents[1]

U. S. 398,101, William Webster. Uses iron electrodes and addition of salt or sea water.

U. S. 937,210, J. T. Harris. Uses a combination of iron and aluminum electrodes, superior clarification is claimed.

U. S. 1,079,377, G. W. Swinburne. No electrode system specified, only required that chlorides be added.

U. S. 1,090,893, C. P. Landreth. Description of system using iron electrodes.

U. S. 1,131,067, C. P. Landreth. Modification of the patent above.

U. S. 1,139,778, C. P. Landreth. Apparatus for sewage treatment.

U. S. 1,146,942. C. P. Landreth. Apparatus for treating sewage.

U. S. 1,222,637, C. P. Landreth. Apparatus for treating sewage.

U. S. 1,378,120, C. P. Landreth. Apparatus for treating sewage.

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U. S. 2,520,703, R. M. Wagner. Method for removal of cyanide from plating waste.

U. S. 2,773,025, H. E. Ricks and W. M. Trigg. Method for removal of cyanides from plating wastes.

British 888,654, J. C. Raine. Method for removal of phenols, thiocyanates and thiosulfates from ammonia reactor liquor.

U. S. 3,035,992, L. R. Hougen. Method for purifying sewage using sea-water dilution.

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1) Copy in project files and reviewed

APPENDIX IV

PASTEURIZING UNIT AND PROCEDURE

APPENDIX IV

PASTEURIZING UNIT AND PROCEDURE

A unit was constructed to meet the specifications set by the Taft Center for pasteurizing and storing secondary effluent. This unit consisted of a 27-gallon galvanized steel drum in which two 40-foot coils of 1/2-inch copper tubing had been positioned against the inside of the drum wall. One coil was connected to a steam supply and the other to a refrigerated brine supply.

A five-gallon carboy of filtered secondary effluent was placed in the unit. The carboy was closed with a rubber stopper containing two glass tubes, one of which extended to the bottom of the carboy. The carboy was clamped down and the drum filled with water. The water jacket was continuously agitated by blowing compressed air through it. The passage of live steam through the coil for 40 minutes raised the temperature of the secondary effluent to 185°F. for the required ten minutes. The steam was shut off and the contents allowed to cool. The water bath and carboy were then maintained at 35-39°F. by a thermoregulator controlling a solenoid valve in the brine line. The temperature of the water jacket was continuously monitored. The carboy was sealed at all times and solution was removed by pressurizing with high purity nitrogen.

Samples have been maintained with this system up to three weeks with little change in analysis. Although it has been reported that this method often precipitates some of the phosphates present, we have not had this problem. In fact, no precipitates of any kind have been observed during storage of filtered secondary effluent.

APPENDIX V

STATISTICAL STUDIES

APPENDIX V

STATISTICAL SERIES - I

1. Summary

A statistically designed experimental sequence of 24 runs was performed in connection with Public Health Contract PH 86-62-113. The independent variables studied were:

A. Initial pH
B. Choice of Electrode Material
C. Current Density
D. Temperature Level

The dependent variables observed were:

1. Change in pH (Δ pH)
2. Change in Cl^- (Δ Cl^-)
3. Change in Chemical Oxygen Demand (Δ COD)
4. Change in Total Solids (Δ TS)
5. Change in Alkylbenzene Sulfonates (Δ ABS)
6. Color

The experimental results demonstrated a high degree of variability; nevertheless, highly significant conclusions could be drawn. Those were:

1. By far the most important independent variable was choice of electrode material. Lead dioxide was the preferred material, giving far better ΔCl^-, ΔCOD, ΔABS, and color than did graphite.

2. Current density (CD) affected only ΔpH: operation at high CD raised pH more than operation at low CD.

3. In addition to the above main effects, two factor interactions* involving electrode material were observed:

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* By "Main Effect" is meant the extent to which one independent variable (such as choice of electrode material) affects one dependent variable (such as change in chemical oxygen demand). If two main effects exist, one should expect each one to affect the dependent variable independently; thus, the effects should be additive. Non-additivity is referred to as "interaction"; interaction may involve antagonism (negative interaction) or synergism (positive interaction).

a. When graphite electrodes were used, increased temperature caused undesirable changes in $\triangle Cl^-$, $\triangle$ COD, and color. These undesirable changes were absent when PbO_2 electrodes were used.

b. Increased current density improved $\triangle$ COD when graphite electrodes were used, but had no effect with PbO_2 electrodes.

4. Initial pH was unimportant.

II. Design of the Experiment (Statistical)

Since four independent variables were to be studied, a sequence of 2^4 or 16 runs was indicated, in a 2-level simple factorial experiment. Because appreciable experimental variability was anticipated, additional runs were desirable to provide a direct estimate of experimental error against which the effects of the independent variables and their interactions might be compared. The sequence decided upon was one of 24 runs, consisting of a 2^4 factorial (16 runs) partially duplicated by a further 2^{4-1} fractional factorial (8 runs) (cf. Dykstra, Technometrics, I, 63-75, 1959).

Because it was believed that a single stock of raw material might change enough in the time interval between running the first and last experiment to render the results questionable, the sequence was blocked into three groups of 8, each group to be run with a different fresh batch of raw material, permitting the effects to be evaluated free from confusion by the raw material chosen, and permitting the effects of change in raw material to be evaluated.

The experimental conditions in each run are indicated in Table I, page 80, as are the levels of the independent variables employed.

III. Methods of Calculation

The contrasts were calculated by the Yates methods, using the G-15 computer and routines previously prepared. The computation of effects and the analysis of variance were performed manually, following the procedure described by Dykstra (loc. cit.). Significance of the effects was determined by the variance ratio or "F" -test at the 95% level, with the variance for error being calculated from the 8 pairs of duplicate runs.

IV. Results

The numerical results reported below are presented in two ways, for the convenience of the reader: first, in terms of dependent variables (to answer the question "How was a given dependent variable affected?") and second, in terms of independent variables (to answer the question "What effects does a given independent variable exert?").

A. By Dependent Variables

1. $\triangle$pH

	Effective Independent Variable	Effect of Changing from Low Level to High Level of Independent Variable
a. C	Current density	+ 1.7 pH units
	Error of measurement (s)	1.0 pH units

2. $\triangle Cl^-$ (Chloride Ion Concentration)

It was desirable to achieve as large a negative value of $\triangle Cl^-$ as possible; i.e., to cause the greatest possible reduction of Cl^- concentration.

	Effective Independent Variable	Effect of Changing from Low Level to High Level of Independent Variable
a. B	Electrode Choice	- 26. ppm
b. D	Temperature	
c. BD	Interaction	

When PbO_2 electrode was used (high B), increase in D had no effect on $\triangle Cl^-$. When the graphite electrode was used, increase in D changed $\triangle Cl^-$ adversely, by 21 (ppm).

At low D, PbO_2 improved $\triangle Cl^-$ by -13 units compared with graphite.

At high D, PbO_2 improved $\triangle Cl^-$ by -34 units, compared with graphite.

Error of measurement (s) 13 (ppm)

3. △COD (Chemical Oxygen Demand)

The most desirable result was a large negative value of △COD.

	Effective Independent Variable		Effect of Changing form Low Level to High Level of Independent Variable
a.	B	Electrode Choice	-90 ppm
b.	C	Current Density	
c.	BC	Interaction	
d.	D	Temperature	
e.	BD	Interaction	

When PbO_2 electrode was used (high B), current density (C) had no effect. When graphite was used (low B), current density improved △COD by -65. At low current density (low C), PbO_2 improved △ COD by -121, compared with graphite. At high C, PbO_2 improved △ COD by -58, compared with graphite.

When PbO_2 was used (high B), temperature (D) had no effect. When graphite was used, increasing D worsened △ COD by +126. At low temperature (low D), PbO_2 improved △ COD by -24. At high temperature (high D), PbO_2 improved △ COD by -155.

Error of Measurement (s) 34 ppm

4. △TS (Total Solids)

None of the variables affected △TS meaningfully.

5. △ABS - (Alkylbenzene Sulfonates)

The most desirable result was a large negative value.

	Effective Independent Variable		Effect of Changing from Low Level to High Level of Independent Variable
a.	B	Electrode Choice	-2.8 ppm
b.	C	Current Density	+0.75 ppm

Error of Measurement (s) 0.79 ppm

6. Color

Color was defined on the scale below:

0 - water - white
1 - yellow
2 - coffee
3 - black

The most desirable result was a large negative number.

	Effective Independent Variable		Effect of Changing from Low Lever to High Level of Independent Variable
a.	B	Electrode Choice	-1.4 (arbitrary: see color scale above.)
b.	D	Temperature	
c.	BD	Interaction	

When PbO_2 was used (high B), D had no effect on color. When graphite was used (low B), increased temperature (high D) increased color by + 1.4. Solutions were always water-white when PbO_2 was used.

B. By Independent Variable

1. pH

The initial pH, variable A, had no effect upon any dependent variable.

2. Choice of Electrode - Variable B

This was the most important variable, having major effects upon $\triangle Cl^-$, $\triangle$ COD, $\triangle$ ABS, and color. As indicated below, variable B interacted with D, temperature, in affecting $\triangle Cl^-$, $\triangle$ COD and color. In the case of $\triangle$ COD, B also interacted with C.

Dependent Variable		Effect of Changing from C to PbO_2 Electrode	Error of Measurement (s)
a. $\triangle Cl^-$		-26. ppm	13. ppm
	At low D,	-13. "	
	At high D,	-34. "	
b. $\triangle$COD		-90. ppm	34. ppm
	At low D,	-24. "	
	At high D,	-155. "	
	At low C,	-121. "	
	At high C,	-58. "	
c. $\triangle$ABS		-2.8"	0.8 "
d. Color		-1.4 (arbitrary)	0.6 (arbitrary)
	At low D,	-0.8 "	
	At high D,	-2.2 "	

3. Current Density - Variable C

This variable affected the final pH and $\triangle$ABS, and interacted with B in affecting $\triangle$ COD.

	Dependent Variable		Effect of Changing from Low to High Current Density	Error of Measurement (s)
a.	Final pH		+1.7 pH units	1.0 pH units
b.	$\triangle$ABS		+0.75 ppm	0.79 ppm
c.	$\triangle$COD	At high B,	0 "	34. "
		At low B,	-65 "	

4. Temperature - Variable D

Of itself, temperature was not an important variable; however, it interacted profoundly with B, electrode choice, as shown below, in affecting $\triangle$ Cl^-, $\triangle$ COD, and color.

Dependent Variable		Effect of Changing from Low to High Temperature	Error of Measurement (s)
a. $\triangle Cl^-$	At high B,	0 ppm	13 ppm
	At low B,	+21 "	
b. $\triangle COD$	At high B,	0 "	34 "
	At low B,	+126 "	
c. Color	At high B,	0 (arbitrary)	0.6 (arbitrary)
	At low B,	+1.4 "	

V. Conclusions

On all counts, PbO_2 is an electrode material preferable to graphite. With PbO_2 electrodes, the temperature level is of no importance. Under these conditions, current density is of little importance; it may be that high current density is slightly less effective than low in reducing ABS content. The initial pH is immaterial.

Experiment on Electrolysis of Sewage - Revised

12/26/62

Table I. Run Conditions

Run No.	Code	Variables	A	B	C	D
1.	ab		+	+	-	-
2.	ad		+	-	-	+
3.	(1)		-	-	-	-
4.	bc		-	+	+	-
5.	bd		-	+	-	+
6.	cd		-	-	+	+
7.	ac		+	-	+	-
8.	abcd		+	+	+	+
9.	acd		+	-	+	+
10.	b		-	+	-	-
11.	c		-	-	+	-
12.	abc		+	+	+	-
13.	abd		+	+	-	+
14.	bcd		-	+	+	+
15.	a		+	-	-	-
16.	d		-	-	-	+
17.	abcd		+	+	+	+
18.	ac		+	-	+	-
19.	cd		-	-	+	+
20.	(1)		-	-	-	-
21.	bc		-	+	+	-
22.	ad		+	-	-	+
23.	ab		+	+	-	-
24.	bd		-	+	-	+

Key

Variables	Levels	
	-	+
A. pH	6	8
B. Electrode	Carbon	PbO_2
C. Current Density	6 ma/cm^2	30 ma/cm^2
D. Temperature	25-30° C.	50-60° C.

APPENDIX V
STATISTICAL SERIES - II

I. Summary

A statistically designed sequence of 12 runs was run as a continuation of the work described in Part I, Appendix V. In this set, the electrode material was platinized titanium; the independent variables were:

A. Initial pH
B. Current Density
C. Temperature Level

The dependent variables were those mentioned in the preceding section, except that color was not studied in the runs discussed here.

Only the initial pH caused significant effects. They were:

1. Starting at a lower pH (acidic) caused pH to fall off sharply; while starting at the high pH level (alkaline) caused pH to rise slightly.

2. Starting at a high pH caused a reduction in total solids; starting at low pH caused total solids to increase.

II. Design of the Experiment (Statistical)

The design was similar to that described in the preceding section differing only in that a single electrode material was used, and only 12 runs were made.

III. Methods of Calculation

The calculations were the same as those covered in the preceding section.

IV. Results

A. Only one independent variable had significant effects: variable A, the starting pH. The effects upon the several dependent variables were:

1. $\triangle_{pH}$

Increasing the initial pH from 5 to 8 caused $\triangle$pH to increase by about + 2.5 pH units. If the solution was alkaline at the start, pH increased only slightly, but if the solution was acidic, pH fell off markedly.

Error of measurement (s) 0.6 pH units

2. $\triangle_{Cl^-}$

No significant effect brought about by initial pH.

Error of measurement (s) 2.5 ppm

3. $\triangle_{COD}$

No significant effect brought about by initial pH.

Error of measurement (s) 12.5 ppm

4. $\triangle_{TS}$

The desired result is a large negative value of $\triangle$TS.

Increasing initial pH from 5 to 8 caused $\triangle$TS to become more negative by 260 ppm.

Error of measurement (s) 24 ppm

5. $\triangle_{ABS}$

No significant effect brought about by initial pH.

B. In the case of $\triangle$ABS, the interaction BC had an effect which, while not significant at the 95% level, still warrants mention. Operation at low B and high C (low current density and high temperature) or vice versa (high current density, low temperature) gave somewhat better values of $\triangle$ ABS than runs when both current density and temperature were high, and when both were low.

V. Further Work

These experiments are combined with the 12 runs previously run using PbO_2 as an electrode material, and analyzed as a whole, to permit reasonably precise conclusions to be drawn as to the relative merits of PbO_2 and platinized titanium electrodes (next section).

APPENDIX V

STATISTICAL SERIES - III

1. Summary

Those runs described in Pt. I which used the PbO_2 electrode were combined with the runs described in Pt. II to form a balanced set of 24 runs, which were analyzed in the same way as the original data, as covered in the first sections of this Appendix.

The results obtained, significant at the 95% level of confidence, were:

1. By far the most important variable was choice of electrode. PbO_2 was the preferred material. It improved reduction in the levels of Cl^-, COD, and ABS. With respect to those dependent variables, the PbO_2 electrode was independent of the other independent variables, temperature, current density, and initial pH.

   Use of PbO_2 resulted in the least change of pH under the following conditions:

   If starting pH was low, low current density.
   If starting pH was high, high current density.

   When PbO_2 was used, there was only a small reduction in TS. When the Pt-Ti electrode was used at high starting pH, a large reduction in TS was observed.

2. Initial pH was an important variable only when the Pt-Ti electrode was used. Under those conditions, the results obtained, consistent with Ref. II., were:

   At low initial pH, pH fell off; at high initial pH, pH increased.

   This effect was accentuated by interaction with current density.

3. Current density in no case exerted a clear-cut main effect. It interacted with initial pH in effecting change in pH, with initial pH and temperature in effecting change in TS, and, in the case of the Pt-Ti electrode only, with temperature in effecting change in ABS. All these interactions were minor though real.

4. Temperature level in no case exerted a main effect. In interaction with current density and initial pH, it affected Δ TS slightly; in interaction with current density for the Pt-Ti electrode, it affected Δ ABS slightly. In both cases the effects were minor.

II. Design of the Experiment - Statistical

One-half the experiments reported in Pt. I (12 in number) employed the PbO_2 electrode; the other variables were:

A. Initial pH	6	8
C. Current Density (ma/cm^2)	6	30
D. Temperature, °C	25-30	50-60

All the experiments reported in Pt. II (12 in number) employed the platinized titanium (Pt-Ti) electrode; the other variables were:

A. Initial pH	5	8
B. Current Density (ma/cm^2)	6	30
C. Temperature °C	25-30	50-60

It is the purpose of this report to combine these two balanced sets of experiments into a single group of 24, characterized below:

A. Initial pH	5,6	8
B. Choice of Electrode	Pt-Ti	PbO_2
C. Current Density (ma/cm^2)	6	30
D. Temperature °C	25-30	50-60

It is obvious at the outset that several objections can be raised to this procedure: First, not all runs were made with the same batch of raw material. This argument may be disposed of by the observation, in the work of both Refs. I and II, that raw material difference, as noted by blocking, was not important. Second, not all runs were made in a single randomized time pattern. The only defense against this claim is the observation that no time-dependent trends were obvious in the course of the earlier work. Third, the low-level of initial pH in runs with PbO_2 electrode was 6, while in runs with Pt-Ti electrodes it was 5. If an interaction is observed between initial pH and electrode choice, especially involving differences in behavior at low pH, it will not be possible to state unequivocally whether this is a true interaction, or merely the effect of pH alone. Any such interaction, if observed, will require careful comparison with the results observed earlier. Fourth, it may be that variability will not be the same for both sets of runs. The reply to this fault is that there is little reason other than differences in electrode material for such change in variability; the purpose of this analysis is to detect all differences attributable to electrode materials.

III. Methods of Calculation

As in Parts I and II, contrasts were calculated by the Yates method on the G-15 computer using standard routines at hand. Computation of effects, sums of squares, and decompostion of sums of squares (as described by Dykstra, loc. cit. in Pt. I) for combinations of main effects, 2-factor and 3-factor interactions, were run on the computer with greatly increased speed and at least equal accuracy, with a new program. Analysis of variance tables for each of the dependent variables were prepared manually, and tests of significance (F-tests) were also run manually.

IV. Results

As in Pt. I, results are presented in terms first, of dependent variables (How was a given dependent variable affected?), and second, of independent variables (What effects does a given independent variable exert?).

A. By Dependent Variables

1. $\triangle$pH

Effective Independent Variable	Effect of Changing from Low Level to High Level of Independent Variable

No main effects were found to be significant.

Interactions:

a. AB	-1.70 pH units
b. AC	1.38 " "
c. ABC	1.20 " "

Standard Deviation of Effects (s_E) = 1.00
Average Value of $\triangle$ pH from all observations = - 0.99 pH unit

Interaction AB: At low B (Pt-Ti electrode), increasing initial pH from 5 to 8 caused the $\triangle$pH to become less negative (effect was +2.5, acc. to Ref. II). At high B (PbO_2 electrode), increasing pH from 6 to 8 caused the $\triangle$ pH to become slightly more negative. At low pH (low H), the Pt-Ti electrode caused a slightly more negative $\triangle$ pH than did the PbO_2 electrode; but at high pH, Pt-Ti electrode caused pH to rise ($\triangle$pH positive) while PbO_2 caused a strongly negative $\triangle$ pH. Thus, while the apparent effect of electrode choice at the lower pH might have been attributable to the lower initial pH employed with the Pt-Ti electrode, the effect at the upper pH level was unequivocal: Pt-Ti caused a positive $\triangle$pH, while PbO_2 caused a strongly negative $\triangle$pH.

Interaction AC: At low current density (low C), increasing the starting pH made $\triangle$ pH more negative; at high current density, increasing the starting pH caused $\triangle$ pH to become slightly positive. When the starting pH was low, $\triangle$ pH became more negative when current density was increased; but when the starting pH was high, $\triangle$pH became slightly positive when current density was increased.

Interaction ABC: At low B (Pt-Ti electrode), change in AC from low to high caused little change in $\triangle$pH. At high B (PbO_2 electrode), change in AC from low to high caused $\triangle$ pH to become much less negative.

Summing up the effects of these interactions AB, AC and ABC, it appears that if the desired result is the smallest change in pH, one should operate as follows:

Pt-Ti	PbO_2
Low starting pH, no effect of current	Low starting pH, low current and high starting pH, high current

2. $\triangle Cl^-$

Effective Independent Variable	Effect of Changing from Low Level to High Level of Independent Variable
a. B, Electrode Choice	-59.8 ppm
Standard Deviation of Effects (s_E)	3.5 ppm
Average Value of $\triangle Cl^-$ from all observations	-33.6 ppm

Thus, PbO_2 caused a far greater reduction in Cl^- than did Pt-Ti.

3. $\triangle TS$

The desired effect is a large negative value of $\triangle TS$.

Effective Independent Variable	Effect of Changing from Low Level to High Level of Independent Variable
a. A, initial pH	-136. ppm
b. AB Interaction	+111. ppm
c. ACD Interaction	- 52. ppm
Standard Deviation of Effects (SE)	18.1 ppm
Average Value of $\triangle TS$ from all observations	+ 13.1 ppm

A effect, AB Interaction: When A was low (low starting pH) use of Pt-Ti resulted in a high positive $\triangle TS$; use of PbO_2 caused a slight positive $\triangle TS$. When A was high (high starting pH), use of Pt-Ti resulted in a high negative $\triangle TS$; when PbO_2 was used, $\triangle TS$ was about 1/5 the value with Pt-Ti.

ACD Interaction: So long as A was high (high starting pH), $\triangle$TS varied only slightly with CD interaction. However, when A was low, $\triangle$ TS was positive; at high CD (both high current density and high temperature or low current density and low temperature) $\triangle$TS was a large positive number.

4. $\triangle_{COD}$

The desired effect was a large negative value of $\triangle_{COD}$.

Effective Independent Variable	Effect of Changing from Low Level to High Level of Independent Variable
a. B, Choice of Electrode	-24.0 ppm
Standard Deviation of Effects	4.0 ppm
Average value of COD from all observations	-35.1 ppm

5. $\triangle_{ABS}$

The desired effect was a large negative value of $\triangle_{ABS}$.

Effective Independent Variable	Effect of Changing from Low Level to High Level of Independent Variable
a. B, Choice of Electrode	- 3.2 ppm
b. BCD Interaction	- 1.0 ppm
Standard Deviation of Effects	0.7 ppm
Average value of $\triangle$ ABS from all observations	- 5.0 ppm

BCD Interaction: At high B (PbO_2 electrode) there is no CD interaction. At low B (Pt-Ti electrode), there is an advantage to working with CD low (i.e., either high temperature but low current density or vice versa).

B. By Independent Variable

1. A - Initial pH

Dependent Variable		Effect of Changing from Low Initial pH to High Initial pH	Avg. Value of Obs'd. Variable	Standard Deviation of Effect
a. ΔTS		-136 ppm	+13.1 ppm	18.1 ppm
Interaction	AB	(+111) "		
	ACD	(- 52) "		
b. ΔpH				
Interactions	AB	(-1.70) pH units	-0.99 pH units	1.00 pH units
	AC	(+1.30) "		
	ABC	(+1.20) "		

2. B - Choice of Electrode

Dependent Variable	Effect of Changing from Pt-Ti Electrode to PbO_2 Electrode	Avg. Value of Obs'd. Variable	Standard Deviation of Effect
a. ΔCl^-	-59.8 ppm	-33.6 ppm	3.5 ppm
b. ΔCOD	-24.0 "	-35.1 "	4.0 "
c. Δ ABS	- 3.2 "	- 5.0 "	0.7 "
Also BCD	(- 1.0) "		
d. ΔTS	----	+13.1 "	18.1 "
AB	(+111.2) "		
e. ΔpH	----		
AB	(- 1.70) pH units	- .99 pH units	1.00 units

3. C - Current Density

No main effect in any case.

Dependent Variable	Effect of Changing from Low Current Density to High Current Density	Avg. Value of Obs'd Variable	Standard Deviation of Effect
a. Δ pH	----	0.99 pH units	1.00 pH units
AC	(+1.38) ppm		
b. Δ TS	---- "	+13.1 ppm	18.1 ppm
ACD	(-52.0)		
c. Δ ABS		-5.0 "	0.7 "
BCD	(1.00) "		

4. D - Temperature

No main effect in any case.

Dependent Variable	Effect of Changing from Low Temperature to High Temperature	Avg. Value of Obs'd. Variable	Standard Deviation of Effect
a. Δ TS		+13.1 ppm	18.1 ppm
ACD	(-52) ppm		
b. Δ ABS		- 5.0 "	0.7 "
BCD	(-1.0) "		

In addition to the results described above, it is of interest to consider the variability of operation with the two electrode materials. Tabulated below are the standard deviations noted for individual runs in Ref. II, applying to the Pt-Ti electrode, and in this analysis, in which the standard deviation reflects primarily the PbO_2 electrode.

Dependent Variable	Standard Deviation of Single Runs	
	Pt-Ti Electrode	PbO_2 Electrode
Δ pH in pH units	0.6	1.0
Δ TS ppm	24.2	59.1
Δ COD ppm	12.7	13.1
Δ Cl^- "	2.5	11.4
Δ ABS "	.9	2.2

It appears that the PbO_2 electrode system is somewhat more variable than that involving the Pt-Ti electrode.

Conclusions

The PbO_2 electrode system, either *per se* or by interaction with other independent variables, affects in a desirable way all the dependent variables studied except TS. It gave satisfactory results essentially without regard to temperature, current density, or initial pH.

APPENDIX VI

COST ESTIMATES

APPENDIX VI

COST ESTIMATES

These estimates comprise:

A. Cost estimates for fresh effluent electrolytic plants of various capacities.

B. Processing costs for fresh effluent.

C. Cost estimates for brackish effluent electrolytic plants of various capacities.

D. Processing costs for brackish effluent.

E. Drawing 6F-A proposed design of the fresh water electrolytic plant.

F. Drawing 9B-A proposed design of a brackish water electrolytic plant.

The following assumptions were used in these estimates:

1. Coulombs/1000 gal.

Low dose	34×10^6

2. Cell voltage:

Current Density ma/sq. cm.	Fresh Effluent	Brackish Effluent (1000 ppm. NaCl)
1	3.3	3.2
6	7.8	5.5
9	---	6.9
30	27.9	14.9

3. Lead dioxide anode size 1 1/4" x 6" x 30"

4. Active anode area 2 sq. ft./anode

5. Anode cost $20.00 each

6. Anode life 1000 days

7. Effluent conductivity

mhos/cm. at 25° C.

Fresh effluent	5×10^{-4}
Brackish effluent*	12×10^{-4}

*1000 ppm NaCl

Notes on estimates:

1. The most economical plant to build and operate for fresh waters was the one with a current density of 6 ma./sq. cm. across the anodes. For the brackish waters, the plant with 9 ma./sq.cm. across the anodes was the most economical. Our studies are based on these two plants.

2. The battery limits for water flow are the feeding trenches along the concrete cell tanks and the discharging trenches on the opposite side of the same tanks. Others must provide the necessary sewers to get the waters to and from these points.

3. The electrification begins with the high voltage primary switch gear.

4. Not included in the estimates are site preparations, roads, landscaping, fences, land, area lighting, laboratories or other buildings.

5. A traveling powered maintenance bridge on set of ground rails is included with each basic plant.

6. For the processing costs, 34×10^6 coulombs per 1,000 gallons was used in computing the power consumption figures.

SECTION A

ESTIMATE

FRESH WATER ELECTROLYTIC PLANT

Current Density - 6 ma./cm.^{2} | Capacity - 2,000,000 gpd

Item	Material	Labor	Total
Excavations		2,400	2,400
Foundations (Electrical Gear)	4,000	3,000	7,000
Electrolytic Tanks (4)	16,000	16,000	32,000
Tank Membranes*	3,000	9,000	12,000
Anodes (72,000)	1,440,000	18,000	1,458,000
Cathodes (72,000)	50,400	18,000	68,400
Anode - Cathode Supports	36,000	18,000	54,000
Primary Sw. Gr., Transformers, Rectifier, D.C.Sw., Metering, Alarms (7,200 KW)	180,000	36,000	216,000
Busses (Main)	35,000	30,000	65,000
Anode - Cathode Connectors	36,000	18,000	54,000
Traveling Maintenance Bridge	15,000	10,000	25,000
Sub Totals	1,815,400	178,400	1,993,800
Contingencies	370,000	36,000	406,000
Total Labor & Material	2,185,400	214,400	2,339,800
Overheads			
Engineering (Not Repetitive)		150,000	150,000

* These membranes are used in the construction of the cement cell tanks to make them waterproof and electrically insulated.

Item	Material	Labor	Total
Contractor's Profit & Overheads		$150,000	$150,000
Supervision		30,000	
Construction Services & Equipment		55,000	
Insurances & Bonds		30,000	
Fee		35,000	
Total Cost of Project			$2,699,800
	Say		$2,700,000

Plant Costs

2,000,000 gpd	$ 2,700,000
10,000,000 gpd	$12,940,000
$2,700,000 + 4 (2,560,000)*	
100,000,000 gpd	$128,140,000
$2,700,000 + 49 (2,560,000)*	

*Since the major part of engineering would be involved in the initial plant, these costs would not be repeated in the plants that followed. If $10,000 is allowed for engineering, additional plants would cost $2,560,000 each.

Section B

PROCESSING COSTS

FRESH WATER TREATMENT

6ma/cm^2

Operating Month	-	30 days
Monthly Treatment	-	60,000,000 Gallons
Power	-	4,404,000 KWH x .005 per KWH - $22,020
Labor		
Operators 288 mhrs./month @ $3.00/mhr.		- $ 864
Maintenance		
Anode Replacement * 2,160 x ($20.00 + .50)		- $45,000
Cathode Replacement 437 x (.70 + .50)		- $ 530
Depreciation		
Plant Investment $2,700,000 less Cathode-Anode		
Investment $1,490,400 - $1,209,600		
$1,209,600 on a 25 year life		- $ 4,000/month
Total Processing Costs per month		- $72,414

Processing Costs per 1,000 gallons

$72,414/60,000 - $1.21

If power cost is $.01 per KWH, total processing cost per month would be $94,434 and the cost per 1,000 gallons would be $1.57.

* Anode replacement based on $\frac{30}{1000}$ of 72,000 for every 30 days at cost of $20.00 each plus $0.50 installation charge.

Section C

ESTIMATE

BRACKISH WATER ELECTROLYTIC PLANT

Current Density - 9ma/cm^2 Capacity - 2,500,000 gpd *

Item	Material	Labor	Total
Excavations		2,400	2,400
Foundations (Electrical Gear)	4,000	3,000	7,000
Electrolytic Tanks (4)	17,200	17,200	34,400
Tank Membranes	2,400	7,000	9,400
Anodes (60,000) *	1,200,000	15,000	1,215,000
Cathodes (60,000)	42,000	15,000	57,000
Anode - Cathode Supports	30,000	15,000	45,000
Primary Sw. Gr., Transformer, Rectifier, D. C. Sw. Metering, Alarms - (6,900 KW)	175,000	35,000	210,000
Busses (Main)	42,000	36,000	78,000
Anode - Cathode Connectors	30,000	15,000	45,000
Traveling Maintenance Bridge	15,000	10,000	25,000
Sub Totals	1,557,600	170,600	1,728,200
Contingencies	320,000	34,000	354,000
Total Labor & Maintenance	1,877,600	204,600	2,082,200
OVERHEADS			
Engineering (Not Repetitive)		150,000	150,000

* See report paragraph 3.13

Item	Material	Labor	Total
Contractor's Profit & Overheads			$ 150,000
Supervision		30,000	
Construction Service & Equipment		55,000	
Insurance & Bonds		30,000	
Fee		35,000	
			$ 2,382,200
Total Cost of Project - Say			$ 2,383,000

Plant Costs

2,500,000 gpd	$ 2,383,000
10,000,000 gpd 2,393,000 + 3 (2,243,000)* =	$ 9,112,000
100,000,000 gpd 2,393,000 + 39 (2,243,000)* =	$ 89,860,000

* Since the major part of engineering would be involved in the initial plant, these costs would not be repeated in the plants that followed. If $10,000 is allowed for engineering, additional plants would cost $2,243,000 each.

SECTION D

PROCESSING COSTS

BRACKISH WATER TREATMENT

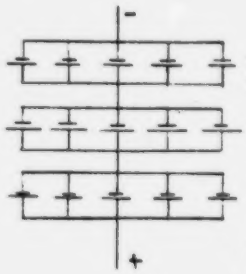
9 ma./cm.^{2}

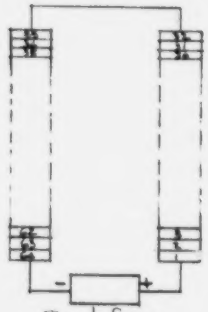
Operation Month	- 30 days	
Monthly Treatment	- 75,000,000 Gallons	
Power	- 4,920,000 KWH x .005 per KWH	= $24,600
Labor		
Operators 288 mhrs./month at $3.00/mhr.		= $ 864
Maintenance		
Anode Replacement 1,825 x ($20 + .50)		= $37,415
Cathode Replacement 365 x (.70 + .50)		= 438
Depreciation		
Plant Investment $2,383,000 less Cathode-Anode Investment $1,242,000 = $1,141,000		
$1,141,000 on a 25 year life		= $ 3,800/month
Total Processing Costs per month		= $67,117

Processing Costs per 1,000 gallons

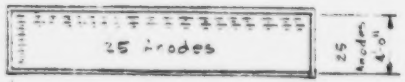
$67,117/75,000 = $.895

If the power cost $.01 per kwh, total processing cost per month would be $91,717 and the cost per 1,000 gallons would be $1.22.





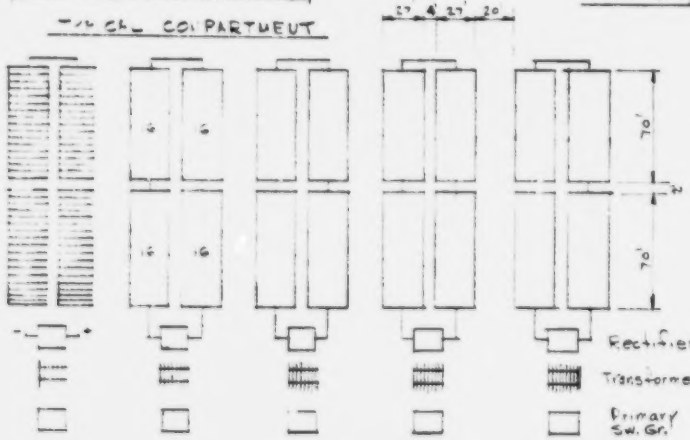
Basic Unit = 2,000,000 Gpd



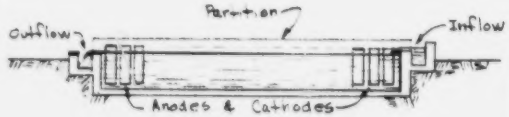
½ CL COMPARTMENT

For 10,000,000 Gpd — 5 Rectifiers Required As Shown

For 100,000,000 Gpd — 50 Rectifiers Required



FLAN - 10,000,000 GPD PLANT



SECTION THRU A COMPARTMENT

FRESH WATER

6 MA/CM² CURRENT D.

APPROVED		APPROVED	
DRAWN		CHECKED	
SCALE		DATE	
APPR. NO.		JOB NO.	

Pennsalt Chemicals ESTABLISHED 1850

DATE	REVISIONS	BY

N° 6F